The Utility of Sedimentary Diatoms as a Measure of Historical Lake pH

by

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ABSTRACT

As a result of increased acid precipitation, the pH of a large number of Canadian Shield lakes has been falling. Prior to this study there was no documentation available to explain the history of lake acidification for the Algoma area lakes. In order to obtain this information the diatom inferred pH technique was developed in this study.

During two field seasons, July 1981 and July 1982, short sediment cores (circa 25-30 cm) were collected from 28 study lakes located north of Lake Superior, District Algoma, Ontario. The surface sediment diatoms (0-1 cm) from each of these lakes were carefully identified, enumerated, and classified in terms of their pH indicator status. The surface sediment diatom analysis indicated that lake pH is one of the most important factors affecting the species composition and relative abundance of diatom populations. Thus diatom assemblages can be sensitive indicators of lake acidification. When Nygaard's index alpha was plotted against observed lake pH, a statistically significant relationship resulted ($r=-0.89$; $p=<0.01$).

The index alpha regression equation was used to construct the pH histories of 4 lakes (lakes X4, CS, U3, and W1). The repeatability of this technique was confirmed by comparing two downcore paleo-pH profiles of Lake W1. These two paleo-pH profiles represented almost identical paleo-pH patterns for Lake W1. The paleo-pH study of Lake X4 revealed that the lake has been rather acidic (pH <5.6) for the last 200 years. It appears that the recent increase in acid precipitation

over the last 30 years has not altered the water pH compared to the lake's pH history. However, the paleo-pH study of another acidic lake (Lake CS) indicated that its pH has significantly dropped over the last 30 years. During this time the Lake CS pH has dropped almost 2 pH units (7.1 to 5.2). The other two lakes studied for downcore pH were circumneutral in nature. One of these lakes (Lake U3) displayed a relatively stable pH history while the other lake (Lake W1) displayed significant pH fluctuations over post-*Ambrosia* time. The variable pH history of Lake W1 was probably associated with the Algoma sintering plant plume and forest fires.

A significant relationship between surface sediment diatoms and observed lake pH and secondly a statistically significant relationship between index alpha and observed pH suggested that diatoms are one of the best indicators of lake pH. Thus diatom inferred pH technique has great potential in explaining the rate of lake acidification.

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INTRODUCTION

1. Acid Rain and its Impact on the Study Area

The growing use of fossil fuels and the use of sulfide rich ores in smelters has resulted in an increased production of sulfur and nitrogen oxides (Robinson 1980). In the atmosphere these oxides react with atmospheric water and after oxidation, yield dilute solutions of sulfuric and nitric acids (Vermeulin 1978; Babich et al. 1980). These acids are removed from the air by acid rain, acid snow, and dry deposition and accumulate in poorly buffered lakes and soils.

A large area of the southeastern Canada and eastern United States receives highly acidic precipitation (average pH 4 to 4.4) (Wright and Gjessing 1976; Likens et al. 1979). This increased acid precipitation has threatend thousands of lakes and streams in acid sensitive areas (Almer et al. 1974; Likens and Bormann 1974). The increased acid precipitation and the resulting acidification of inland water and soil has become one of the most serious environmental problems in North America (Davis et al. 1978; Dillon et al. 1978; Scheider et al. 1979).

The lake acidification in Ontario was first documented as early as 1960 in the vicinity of the Sudbury area (Gorham and Gordon 1960). The lakes in this area are under immense pressure from sulfur oxides and during the 1960's and 1970's they were acidifying at a rate of 0.05 to 0.10 pH unit every year (Wright and Gjessing 1976).

Freshwater in areas characterized by a geological environment that is highly resistant to chemical weathering is extremely vulnerable to inputs of acid precipitation (Wright and Gjessing 1976; Groterud 1981). In these areas, the lakes usually have low concentrations of major ions (specific conductance less than 50 µmhos/cm), and therefore, little buffering capacity. These lakes receive a major portion of their total ion supply from atmospheric precipitation (Gorham 1958).

The detrimental effects of acid rain have been well studied on aquatic ecosystems and in particular the extinction of fish populations has become very obvious (Beamish and Harvey 1972; Beamish 1974; Beamish et al. 1975; Harvey 1975). In addition to fish populations, other aquatic assemblages such as plankton and periphyton have also been observed to change in species composition due to increased acid precipitation (Kwiatkowski and Roff 1976; Yan and Stokes 1976; Yan 1979). These changes could result in serious and some times extreme degradation of the aquatic ecosystem, and the situation can become much more serious if the acid sensitive lakes are in close proximity to metal smelters (Gorham 1976) due to the enhanced solubility of heavy metals at low pH.

A significant relationship has been established between the increased acid precipitation and the chemical composition of acid sensitive lakes of the Algoma District, north of Lake Superior (Coker and Shilts 1979). On the basis of local geology, the water bodies of this area have been identified as extremely susceptible to increased acid precipitation (Coker and Shilts 1979; Thompson 1980; Fortescue et al. 1981). Although the acid precipitation rates and the resulting changes in the water chemistry are not precisely known, in the past 20-30 years the precipitation acidity of this area has been considerably increased.

During 1981 the mean annual precipitation pH in the Wawa area (District Algoma) was 4.16 (Kerr 1982). At normal atmospheric levels of carbon dioxide, the pH of rain water is 5.6 (Likens et al. 1979). When compared with the pH of the natural rain water, the precipitation in Wawa area is as much as one hundred times more acidic. Precipitation of acid rain below 4.7 greatly accelerates the lake acidification process (Wright and Gjessing 1976), and the lakes having alkalinity equal or less than 10 mg/l as $CaCO_3$ are highly sensitive to acidification (Altshuller and McBean 1979; Kerr 1982).

In soft-water lakes, bicarbonates provide most of the buffering capacity and the pH of these waters moves rather slowly towards a value near pH 6.0, but when this value reaches close to 5.5, the bicarbonates are replaced by sulfates and rapid acidification is evident (Wright and Gjessing 1976). This is the most evident reason why in acid stressed environments, lake pH below 5.5 is so common (Wright and Gjessing 1976; Kerr 1982).

The acid sensitive lakes can be differentiated into two major types: a. brown coloured humic lakes and, b. clearwater lakes (Fortescue et al. 1981). Following increased acid precipitation, the unbuffered clearwater lakes frequently become acidic, while the humic lakes are apparently less susceptible to acid rain due to their relatively better buffering capacity (Stewart and Wetzel 1981; Van Dam et al. 1981; Ciolfi in prep.).

The overall chemical composition of lake water results primarily from interaction of the chemical component of precipitation with minerals and organisms in the drainage basin as well as the additional reactions occurring in the lake water itself (Kramer and Tessier 1982). In the Algoma lakes, the pH is generally governed by three factors as noted by Kramer (1975) for the Sudbury area lakes (Coker and Shilts 1979). These are: 1. the rate of input of strong acids; 2. the location of the lake relative to the prevailing wind, which can modify 1; and 3. the geochemistry of the surficial sediments which determines the buffering capacity of the lake and runoff water entering it.

The last factor can override all others; that is, local calcareous soils or carbonate-rich materials can assimilate hydrogen ions and can therefore continue to provide a buffering system for waters located in the acid sensitive areas (Dillon et al. 1978). Hence, in order to know the potential buffering power of any particular lake, it is extremely important to estimate the carbonate content of the glacial material present in the watershed and in buried valleys which underlie lakes in the Canadian Shield (Fortescue et al. 1983).

The topography of the area also has considerable influence on lake acidification. Head water lakes and streams confined in igneous and metamorphic rocks, or where the watershed is covered by thin soil and precipitation is heavy, are especially susceptible to acidification (Gorham and McFee 1980; Kramer and Tessier 1982). Furthermore, the existing buffering capacity of the lake water, mean depth, and the watershed and lake area are also important factors that will determine the eventual effects of acid rain on any lake (Dillon et al. 1978).

In the drainage basin the chemical weathering and ion exchange help to neutralize the incoming acids (Wright and Gjessing 1976). Both of these processes retain hydrogen ions and at the same time release cations. In brief, the retention and increase of hydrogen ions in a watershed is directly related to the net loss of calcium, magnesium, and other cations (Gjessing et al. 1976).

The lake watershed can gradually lose its buffering capacity in two ways: 1. due to the reduction in base saturation of the soil and/or 2. due to the reduction in the contact with acid neutralizing rock material (Groterud 1981). The reduction in base saturation could be the result of continuous runoff of acid water and the reduced contact (both in time and space) may be due to changed hydrology, such as increased precipitation or snowmelt, which can result in the greater amount of runoff from the topsoil.

Due to an increase in acid precipitation, a large number of lakes are also suffering from the higher levels of heavy metals in their water columns and sediments (Scheider et al. 1975; Beamish 1976; Gorham 1976). The elevated heavy metals are mainly the result of direct deposition of metals in precipitation, especially in areas near the base-metal smelters such as Sudbury, Ontario. In the lakes of the Sudbury region heavy metal concentrations are a hundred times higher than the unaffected lakes of southern Ontario (Schieder et al. 1975; Beamish 1976; Gorham 1976; Nriagu et al. 1982).

In addition to direct deposition, the increased metal levels in acidic lakes are also due to the acidification of soil and surface waters (Henriksen and Wright 1978). In soil, the heavy metals are usually present in colloidal forms and are not soluble in water, but excess amounts of hydrogen cations introduced by acid precipitation release these metals from the soil (Tyler 1978). The mobilized heavy metals from the watershed finally enter into the aquatic system, either by surface runoff or movement through the soil to the subsurface waters, and ultimately damage the fauna and flora (Babich et al. 1980).

Dillon et al. (1979) explained that due to the increased acid precipitation, the major ions such as SO_4, Ca, Mg, Na, K were substantially increased in acidic lakes. The study of New England lakes also demonstrated that as the precipitation became more acidic the levels of copper and lead in the lake's sediments increased and the levels of zinc, iron, calcium, magnesium, potassium, and manganese decreased (Norton et al. 1981). Although the increased movement of aluminum ions through soils into lakes and streams has been well documented in the literature (Gjessing et al. 1976; Dickson 1978; Cronan and Schofield 1979), in New England lakes, Norton et al. (1981) did not get any significant relationship between the aluminum contents of the lake sediments and the increased acid precipitation. In the acid runoff waters, the aluminum has been defined as the second most important cation after calcium (Dickson 1978). Above a pH of 5.5, the solubility of aluminum is very low. The aluminum levels in acidified lakes may be 10 to 50 times higher than in circumneutral lakes of the same region (Cronan and Schofield 1979). In addition to the toxic effects on the flora and fauna of these lakes, the elevated aluminum levels also act as a very efficient precipitator for humic substances (Dickson 1978). As a result, humic lake transparency usually increases as it becomes more acidic.

In the Algoma district the anthropogenic sulfur dioxide and subsequent acid precipitation has been identified as both local and long range (Coker and Shilts 1979). Locally, the Algoma Ore Division smelter at Wawa emits about 141,000 tonnes of sulfur dioxide each year (Govt. of Canada 1981). The present levels are considerably higher than the 100,000 tonnes reported in 1960 (Gordon and Gorham 1963). The smelter is considered the seventh largest point source of sulfur dioxide in Canada (Govt. of Canada 1981).

The southwesterly winds from Lake Superior carry the Wawa plume toward the Magpie Valley, northeast of Wawa (Kerr 1982). Extensive vegetation and surface water damage have been caused up to a distance of 50 km from the point source (Gordon and Gorham 1963; Gorham 1976). The repeated exposures to sulfur dioxide has resulted in a fume kill zone of 900 square km (Stinnissen 1975). From this area, birch, spruce, and pine have all been eliminated.

In addition to local sources, a number of pollutants including sulfur dioxide have been reported to be transported from the northeastern United States, particularly from the Ohio Valley and the Midwest (Coker and Shilts 1979; Shannon and Voldner 1982).

2. Diatoms as Paleoindicators

Paleolimnologists investigate the origin and geomorphic history of lake basins and the response of the lakes in them to climate and to changing inputs of water (Frey 1974). In addition to the lake basin and its water, paleolimnologic study also includes the whole watershed area which drains into the lake and as well as its surrounding atmosphere.

Lacustrine sediments accumulated in the lake basin are the result of complex series of chemical, physical, and biological processes occurring within the lake and watershed. Thus the resulting chemistry, mineralogy, and structure of the sediment reflect the depositional environment. Moreover, the morphological and the biochemical remains of organisms in the sediments give insight into past communities, and ecosystems and their biological processes (Frey 1969).

Merilainen (1971) indicated that 3 conditions must be met before one can make valid paleolimnological interpretations: 1. the organisms accumulated in the sediments should come from the lake ecosystem, 2. the remains of the different communities should be completely mixed before the final sedimentation, and 3. the preservation of the remains should be resonably good.

Unfortunately in lake sediments only a few algal groups have left reliable fossil records with which to construct a view of the paleolimnological environment. Among these indicator organisms, the diatoms rank among the best. Diatom stratigraphy which explains the accumulation of diatom frustules in sediments has often been used as evidence of past changes during lake ontogeny (Nygaard 1956; Bradbury and Winter 1976; Brugam 1978; Munch 1980).

The concentration of diatoms in lake sediment cores is closely related to lake sedimentation rate (Round 1964; Bradbury 1975). High sedimentation rates may dilute the accumulation of diatoms, while simultaneously protecting them from destruction by bottom feeding organisms or by dissolution in alkaline lakes (Bradbury 1975).

Bradbury (1975) described five major factors which make diatoms important microfossils in paleolimnological studies:

1. Preservation: The Diatom frustules are made of silica, and hence they can preserve well in the lake sediments while other algae are destroyed. Well preserved diatom frustules have been found in a sequence from late-glacial times to the present day and also in interglacial and preglacial deposits (Round 1964). Holt and Winston (1962) explained the presence of diatom remains as far back as the Jurassic period, and throughout the Mesozoic and Cenozoic eras.

The diatom frustules deposited in lake sediments can be physically or chemically eroded. For example, long thin diatoms such as *Fragilaria crotonensis* and *Asterionella formosa* are rarely found intact. Moreover, diatoms brought into lakes by streams are often broken and eroded (Birks and Birks 1980). Diatom frustule dissolution can also occur in very alkaline conditions. Round (1964) discussed the frustule dissolution problem and concluded that this is not a major factor affecting fossil diatom assemblages in acid and neutral pH lake sediments. However, in the marine environment up to 75% of the frustules may be affected by dissolution. Some times this occurs even before they reaching the ocean's bottom (Round 1964).

2. Abundance: In freshwaters the diatoms are usually present in large quantities and may be a major constituent of lake sediments. For example, in Lake Shagawa, Minnesota, the diatoms formed almost 30% of the dry sediment weight (Bradbury 1975).

3. Ecological diversity: In North America and Europe, more than 1,000 common planktonic and benthic freshwater diatom species have been reported (Bradbury 1975). These diatoms have special preference for a variety of different habitats and environmental conditions. On the basis of their ecological preference, diatom analysis can provide insight into the past conditions of pH, water hardness, salinity, and productivity and responses to eutrophication (Frey 1974). Koivo and Ritchie (1978) analyzed modern diatom samples from the 20 lakes along a transect from northern boreal forest to tundra near the Mackenzie Delta in Canada. They found that most of the diatom assemblages were characteristic of oligotrophic lakes, but different assemblages were found in saline, meromictic, hardwater, and nutrient enriched lakes, confirming water chemistry as an important factor controlling diatom species composition.

4. Identification: The diatom identification is based on the morphological features of their frustules. Therefore, sedimentary diatoms can be identified as accurately as the living ones.

5. Quantification: Generally the fossil remains of diatoms can be easily related to the organisms that produced them. The counts of fossil frustules, therefore, provide direct information about the population and community density of these algae.

3. Diatoms as pH Indicators

Since accumulated diatom frustules in lake sediments represent a time averaged history of the lake environment (independent of seasonal variations), the relative shift in the dominant diatom species indicates an overall shift in lake water chemistry. The presence and abundance of a number of diatom species in a lake is controlled in part by lake pH, and hence the diatom analysis can become an important tool in ascertaining the rate of lake acidification (Berge 1975, 1980; Davis and Berge 1980; Del Prete and Schofield 1981; Dickman in Fortescue et al. 1981; Norton et al. 1981; Renberg and Hellberg 1982; Dixit in Dickman et al. 1983).

The shift in diatom species as lake pH shifts was also described by Berge (1975) in Scandinavian lakes and Van Dam et al. (1981) in Dutch moorland pools (shallow oligotrophic soft water lakes). These authors compared previously collected diatom samples with recent ones and found a significant shift in the diatom populations. In North America, similar observations were reported from the 26 Nova Scotian lakes studied by Vaughan et al. (1982).

In autecological and paleolimnological studies the use of diatoms as pH indicators was primarily recognized by Hustedt (1938) when he proposed the first pH classification scheme for freshwater diatoms. He classified them into five categories.

Alkalibiontic: Occurring at pH values above 7.

Alkaliphilous: Occurring at pH values about 7, and with widest distribution at pH above 7.

Indifferent : Equal occurrence on both sides of pH 7.

Acidophilous : Occurring at pH about 7, and with widest distribution at pH values below 7.

Acidobiontic : Occurring at pH values below 7, optimum distribution at pH 5.5 or less.

Hustedt (1938) tried to distinguish various pH intervals much more precisely by using his pH spectrum. On the basis of major diatom forms (contributing 10% or more of the total number of individuals), he defined the following pH intervals :

pH value above 7: The frequent forms consist almost exclusively of alkalibiontic and alkaliphilous together with indifferent forms.

pH 6-7: The majority consist of alkaliphilous species which begin to disapper within this interval, the indifferent forms are frequent, whereas about 30% of the frequent forms represent acidophilous species.

pH 5-6: Alkaliphilous and indifferent forms much less numerous, the frequent forms have up to 75% acidophilous and acidobiontic diatoms.

pH 4-5: Alkaliphilous forms have disappeared, the indifferent diatoms still comparise 20% of the frequent forms, whereas about 80% of the diatoms are acidophilous and acidobiontic.

pH less than 4: The number of diatoms is drastically reduced. Those that remain are exclusively acidobiontic.

Nygaard (1956) traced the pH history of Lake Gribso up to the Atlantic Period with the help of Hustedt's (1938) pH spectra and the commonly accepted hypothesis that the relative frequency of different diatom species in the lake sediments depends on the pH of the lake water at the time when the sediments were deposited.

Nygaard (1956) explained that since Hustedt's pH classification is based on 5 equally possible variables, the relationship between the diatom spectrum of the sample and the pH of the water can not be quantified. He criticized the quantitative concept of Hustedt's ecological system and suggested that it is better to take into consideration all the species present because it must be assumed that some rare diatoms may give as much information as some abundant ones. Thus every species contributes significantly to the total diatom species population. However, since the contribution of each species is limited by its relative frequency, extremely rare species receive a correspondingly smaller recognition.

Nygaard (1956) indicated that the acidobiontic and alkalibiontic species are better pH indicators than the acidophilous and the alkaliphilous diatom species respectively. Consequently, he emphasized that the acidobiontic and alkalibiontic diatom species should be assigned a larger numeric value in statistical calculations than the acidophilous and alkaliphilous diatom species. He introduced a quantitative measurement by producing the following three indices:

$$\text{Index Alpha} = \frac{\text{acid units}}{\text{alkaline units}}$$

$$\text{Index Omega} = \frac{\text{acid units}}{\text{number of acid taxa}}$$

$$\text{Index Epsilon} = \frac{\text{alkaline units}}{\text{number of alkaline taxa}}$$

Where the acid and alkaline units can be computed by multiplying the relative frequency of acidobiontic and alkalibiontic species by five and then adding this to the relative frequencies of acidophilous and alkaliphilous diatom species. The arbitrary coefficient "5" is an ecological significant number for acidobiontic and alkalibiontic diatom species.

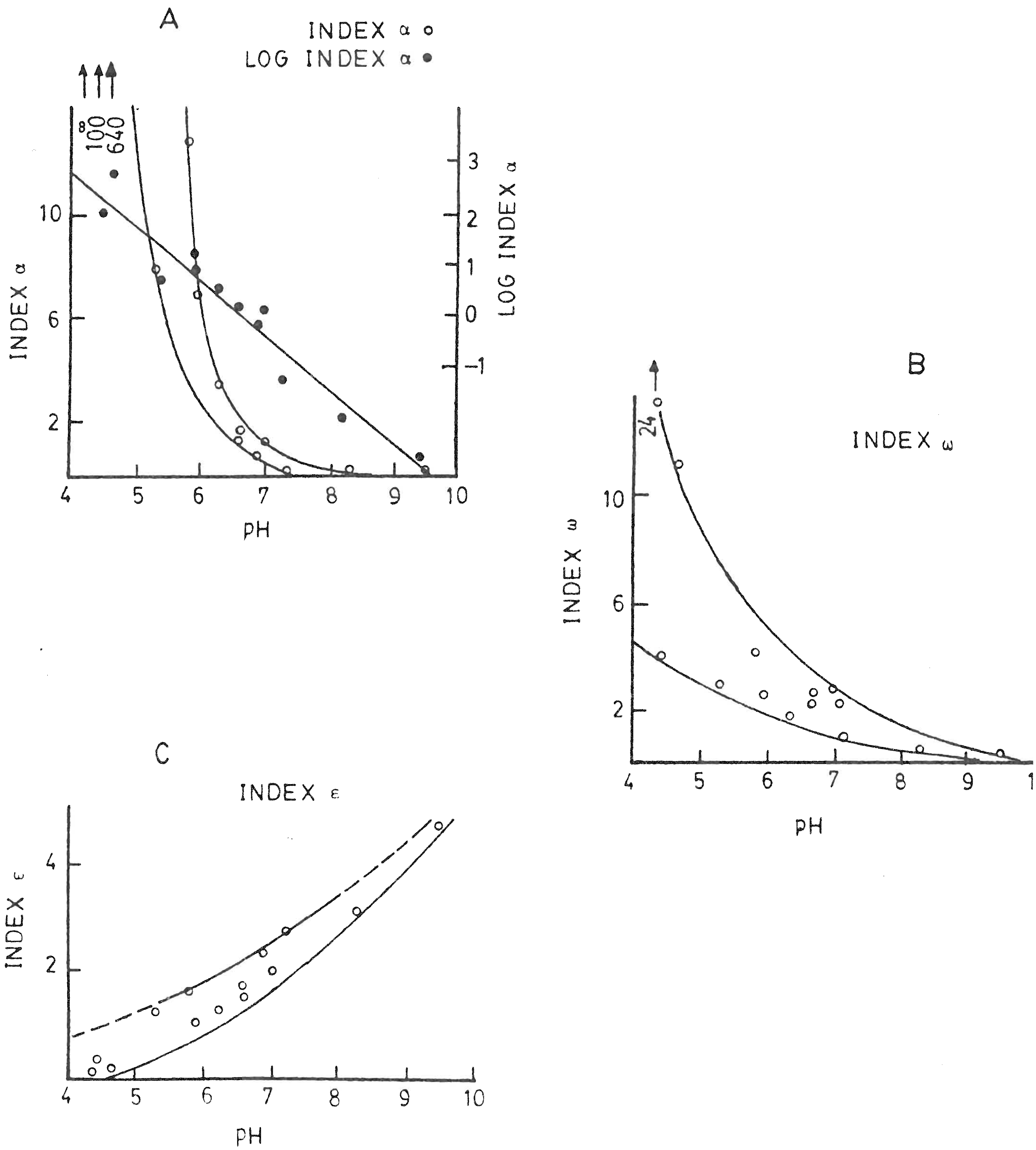
Nygaard (1956) further tried to correlate the living diatoms of Danish brown waters and the pH ranges from where they were collected. He observed that the index alpha values were extremely high for the diatom samples collected from the strongly acid waters (pH never attaining the value 5.5). Similarly, in constantly alkaline waters (pH value 9.0 or more) the index alpha values were extremely low (0.003). On the basis of limited available data, he asserted that an index alpha value of about 15 corresponds to a pH range 5.0-6.5.

The importance of Hustedt's (1938) and Nygaard's (1956) method was later established by Merilainen (1967), when he clearly correlated the observed lake pH results with the surface sediment diatom assemblages of 14 Finnish lakes and ponds (pH range 4.3 to 9.4). He noted that Hustedt's pH spectra gives fairly good information about the hydrogen ion concentration of the water. However, he indicated that the pH limits and the names of the pH groups should not be interpreted too strictly, as the actual assignment of diatoms to pH categories is too loose to permit such strict interpretations.

When Merilainen (1967) computed and plotted the results of Nygaard's indices as a function of observed lake pH (Fig.1), his results confirmed the significance of Nygaard's paleolimnological method. He recognized the importance of index alpha and noted a linear relationship between log alpha and observed pH. In Merilainen's study the index alpha results approached zero at pH > 7.5 and infinity at pH <4.5. He explained that index alpha values were naturally low in alkaline waters, but even there the relationship with pH was still good. An accuracy of around one pH unit can be achieved by using this method according to Merilainen (1967). However, recent improvements have allowed even greater resolution (Del Prete 1981; Dickman in Fortescue et al. 1981; Norton et al. 1981; Dixit in Dickman et al. 1983).

Digerfeldt (1972) used index alpha and epsilon to evaluate the pH changes in a 7 meter long sediment core from Lake Trummen. He considered index alpha to be the most reliable of the three indices because the calculation of index omega and epsilon was based on the number of species prefering different pH groups. Digerfeldt (1972) concluded that although the index alpha gives slightly elevated pH results, they are still very close to the correct pH values.

Figure 1. The relationship between observed pH and Nygaard's 3 indices (Merilainen 1967).


A
INDEX α ○
LOG INDEX α ●
INDEX α
LOG INDEX α
pH
B
INDEX ω
INDEX ω
pH
C
INDEX ε
INDEX ε
pH

Almer et al. (1974) evaluated the effect of lake acidification on plankton communities by looking at the downcore diatom profile of an acidified Swedish lake. They reported a significant decreaes in the frequency of diatom frustules from older to recent sediments along with an increase in the proportion of acidobiontic diatoms in the recent sediments.

Berge (1975) used the Nygaard's omega index (1956) and Merilainen's curve (1967) to infer the 800 years pH history of Lake Langtjeron, Norway. The study revealed that the recent increase in acid precipitation has not caused any significant change in lake pH. Thus the lake was naturally acidic over the last 800 years (pH around 5.0). Berge (1975) evaluated the importance of the omega index and found that the index was sensitive to variations in the number of species present in the sample. According to him, the more reliable expressions for the pH developments in the lake can be obtain by comparing the calculated pH intervals with the relative distribution of the total diatom flora in the sediment core.

In Norway, Davis and Berge (1980) analyzed the surface sediment diatoms of 24 lakes of different pH and inferred the past pH history of 2 lakes. This was done with regression coefficients derived from the surface sediment diatom analysis. The coefficients were later applied to downcore diatom samples to construct their downcore pH profiles.

Del Prete and Schofield (1981) and Norton et al. (1981) used the index alpha and observed a linear relationship between the log alpha and observed pH. The results were very similar to those of Merilainen (1967). They used the regression equation obtained from the surface sediment diatom analysis for calculating the historical lake pH. Both of these studies supported the basic idea that the pH indices based on the diatom microfossils are realistic indices of the rate of lake acidification.

To overcome the problem associated with the very high index alpha results in extremely acidic waters described by Merilainen (1967) and Norton et al. (1981), Renberg and Hellberg (1982) modified the index alpha and generated a new index for computing the diatom inferred pH (Index B).

$$\text{Index B} = \frac{\%\ \text{ind} + 5 \times \%\ \text{acp} + 40 \times \%\ \text{acb}}{\%\ \text{ind} + 3.5 \times \%\ \text{alp} + 108 \times \%\ \text{alb}}$$

Where as acb = acidobiontic

acp = acidophilous

ind = indifferent or circumneutral

alp = alkaliphilous

alb = alkalibiontic

4. Research Purpose:

The purpose of this study was to test the reliability and sensitivity of diatoms as pH indicators in Canadian Shield Lakes, north of Lake Superior, District Algoma, Ontario. The study was necessary to explain the pH history and subsequent acidification in selected Algoma lakes.

DESCRIPTION OF STUDY AREA AND STUDY LAKES

1. Study Area

A study area north of Lake Superior, District Algoma, Ontario was selected for this study (Fig.2). The area covered was about 11,250 square kilometers. Many lakes in this area are seriously affected by acid rain and their pH has considerably dropped in the past few decades (Fortescue et al. 1981; Kerr 1982). Within the study area the 1981 mean annual precipitation pH was 4.16 (Kerr 1982).

The study area lies within the Canadian Shield. It is underlain by ancient sedimentary, igneous, and metamorphic rocks formed in Precambrian time (Pye 1969). The most common rock types are granitic, volcanic, volcaniclastic and sedimentary (Fortescue et al. 1981). The part of the study area north of Wawa is well buffered by a sheet of sandy calcareous till and glaceolacustrine sediment transported southward from the carbonate bedrock of the Hudson Bay Lowland (Boissonneau 1966; Coker and Shilts 1979). The area south of Wawa is poor in mineral contents and the majority of the lakes in this area are acidic. Fortescue et al. (1981) summarized the geology of the study area as variable and mainly dependent on the bedrock type and glacially transported material.

2. Study Lakes

The 28 lakes selected for this study are shown in Fig.3. Since most of the lakes were unnamed, artificial names (letters) were assigned to them. In most cases the selection was done on the basis of the absence

Figure 2. The location of the study area north of Lake Superior, District Algoma is shown by 150 km long and 75 km wide rectangale. The position of X4, CS, U3, and W1 lakes is noted inside the rectangle.

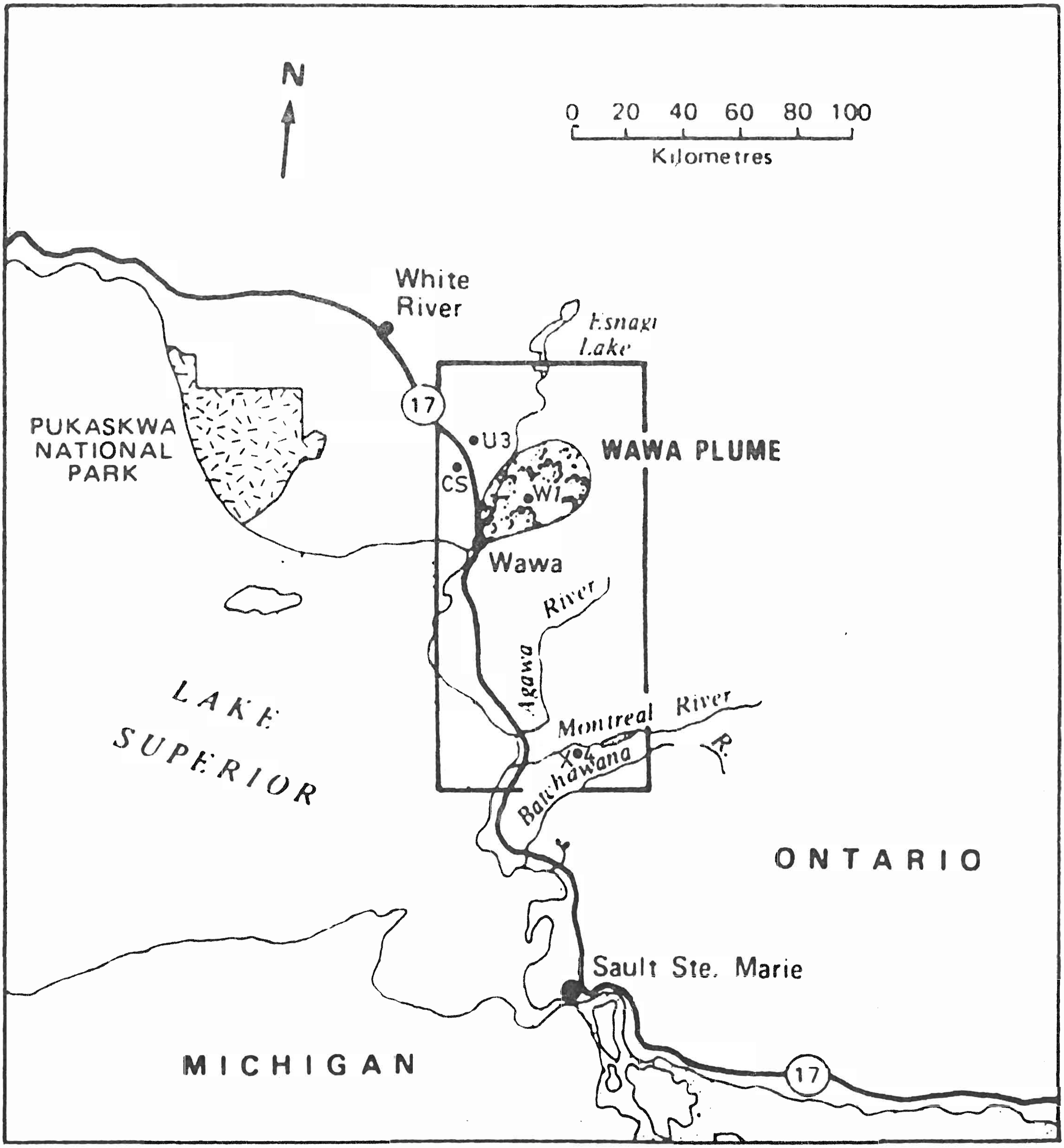
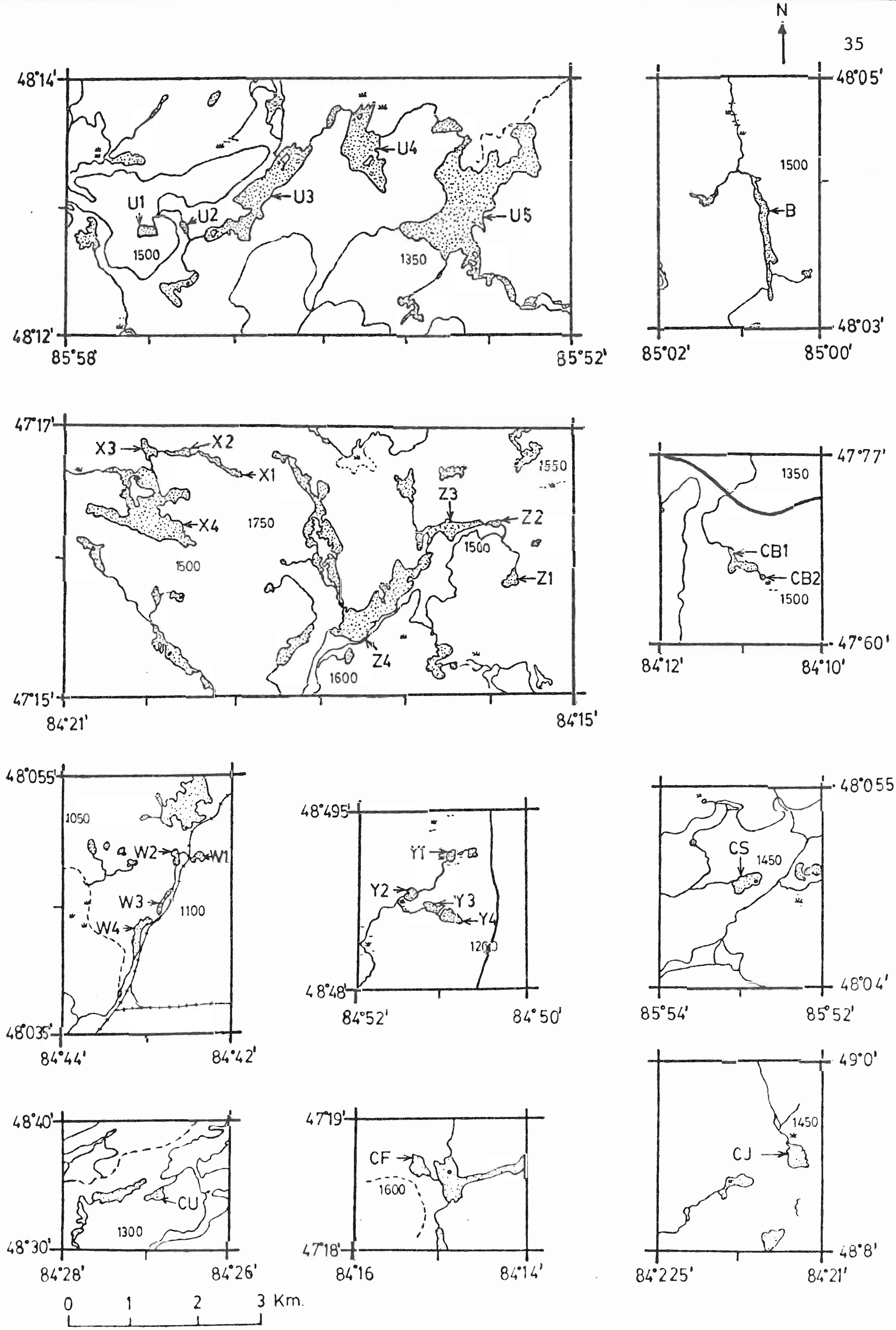

N
0 20 40 60 80 100
Kilometres
White River
17
Esnagi Lake
PUKASKWA NATIONAL PARK
U3
CS
W1
WAWA PLUME
Wawa
River
Agawa
LAKE SUPERIOR
Montreal River
R.
Batchawana
ONTARIO
Sault Ste. Marie
MICHIGAN
17

Figure 3. The location, size, and shape of 28 study lakes located in the Algoma District, north of Lake Superior.


N
48°14'
48°12'
85°58'
85°52'
U1
U2
U3
U4
U5
1500
1350
48°05'
48°03'
85°02'
85°00'
1500
B
47°17'
47°15'
84°21'
84°15'
X1
X2
X3
X4
Z1
Z2
Z3
Z4
1750
1500
1500
1550
1600
47°77'
47°60'
84°12'
84°10'
1350
CB1
CB2
1500
48°055'
48°035'
84°44'
84°42'
1050
1100
W1
W2
W3
W4
48°495'
48°48'
84°52'
84°50'
Y1
Y2
Y3
Y4
1200
48°055
48°04'
85°54'
85°52'
CS
1450
48°40'
48°30'
84°28'
84°26'
CU
1300
47°19'
47°18'
84°16
84°14'
CF
1600
49°0'
48°8'
84°225'
84°21'
1450
CJ
0
1
2
3 Km.

of significant human activity within their watersheds. The majority of the study lakes were not accessible by road. The remoteness of these lakes was necessary to avoid cottage development effects. Acid loading in the area was primarily atmospheric in nature.

The lakes ranged in pH from 4.40 to 8.13, alkalinity -0.51 to 113.5 mg/l as $CaCO_3$, conductivity 19 to 221 µmhos/cm, Secchi disk transparency 1 to 6 meters, elevation 328 to 500 meters, and surface area from 0.02 to 0.63 km^2. The selective physical and chemical features of these lakes are presented in Table 1. It is important to note that no previous physico-chemical record was available for the sets of lakes selected for this study.

For most of the lakes, the watershed topography was rough and the soil was generally thin. The watersheds were well forested except for the W watershed. The study area was populated by maple, white and yellow birch, mountain ash, poplar, black and white spruce, white pine, willow, and cedar (Dickman in Fortescue et al. 1983). The lake surroundings were often steep and the littoral macrophyte vegetation was generally moderate to sparse.

3. Detailed Description of X4, CS, U3, and W1 Lakes

A. Lake X4 (Barbara Lake, 84° 20'W, 47° 165'N)

The Lake X4 had the largest surface area (0.63 km^2) and watershed area (4.51 km^2) among the 4 lakes selected for the detailed study. The lake shorline was rocky and several islands were visible in the lake. The bedrock geology was granitic and the surface deposits were

Table 1. Selective physical and chemical characteristics of the 28 study lakes.

Lake name	pH	* Alkalinity: mg/l CaCO3	* Ca ppm	* SO4 ppm	Conduct. umhos/cm	Secchi depth (m)	* Colour	Maximum depth (cm)	Altitude (m)	* Lake area (km^2)	* Watershed area (km^2)	* Bedrock geology
CB1	4.40	-01.59	00.4	06	020	1.1	humic	01.3	480			granite
X2	4.48	000.70	01.2	05	024	2.0	slightly humic	04.5	437	0.03	1.10	granite
X3	4.58	001.15	01.2	05	021	2.0	slightly humic	08.0	434	0.04	1.25	granite
X1	4.65	001.20	01.4	05	025	1.5	slightly humic	01.5	439	0.05	1.10	granite
CB2	4.70	-00.83	00.6	05	025	1.6	humic	02.0	483			granite
X4	4.80	001.15	01.2	05	022	6.0	clear	14.0	430	0.63	4.51	granite
Z1	4.93	001.25	01.4	05	021	2.5	humic	06.0	500	0.04	0.37	greenstone/granite
B	5.20	-00.51	01.8	09	026	3.0	humic	03.5	483			greenstone/granite
Z3	5.20	001.30	01.6	05	023	2.7	humic	09.0	334	0.02	2.74	greenstone/granite
CS	5.20	001.56	04.4	11	046	4.2	clear	11.0	468	0.09	1.80	greenstone/granite
Z4	5.28	002.00	01.6	05	024	5.2	clear	10.0	430	0.47	9.46	greenstone/granite
CF	5.30	005.38	01.6	08	024	4.8	clear	07.2	516			greenstone/granite
Z2	5.48	001.90	01.6	05	022	2.6	humic	06.6	437	0.02	1.31	greenstone/granite
CU	5.80	000.40	02.0	05	019	4.1	clear	07.1	419			greenstone
CJ	6.20	003.69	03.6	11	044	1.3	humic	01.7	468			greenstone
U1	6.33	008.75	04.2	08	040	1.2	clear	02.0	463	0.04	0.32	greenstone
W1	6.66	013.26	21.0	57	079	2.3	clear	02.3	337	0.02	0.19	greenstone
W2	6.68	013.50	19.8	50	153	4.5	clear	07.0	334	0.02	0.39	greenstone
U5	6.85				054	3.0	clear	13.0	415			greenstone
W3	6.95	015.50	20.0	50	165	1.8	clear	01.8	331	0.02	0.90	greenstone
U2	6.97	032.50	12.2	08	066	2.2	humic	02.2	439	0.02	0.86	greenstone
U3	7.05	016.60	07.4	11	060	2.8	very humic	10.0	430	0.58	4.25	greenstone
U4	7.05	013.92	06.2	05	053	2.0	humic	10.0	422	0.46	7.38	greenstone
W4	7.13	018.25	21.4	53	171	2.0	clear	02.0	328	0.07	1.56	greenstone
Y1	7.78	084.50	21.4	05	168	1.0	clear	01.0	422	0.03	0.93	granite **
Y3	7.80	063.50	18.2	05	135	2.5	slightly humic	02.5	419	0.02	1.92	granite **
Y2	8.05	113.50	32.6	05	142	2.5	slightly humic	04.0	421	0.02	1.37	granite **
Y4	8.13	108.50	28.8	05	221	1.4	clear	01.4	417	0.07	4.43	granite **

* Data adopted from Fortescue et al. (1983).

** Overlain by thick layer of calcarious drift.

discontinuous (Fortescue et al. 1983). The regional geological information compiled by Pye (1969) indicated that the Lake X4 watershed geology is characterized by ancient acidic lava.

The lake water was clear and the Secchi was visible up to a depth of 6 meters. The surface water pH was 4.80 and the alkalinity was 1.15 mg/l as $CaCO_3$. The maximum depth at the sampling site was 14 meters. The physical and chemical features of Lake X4 are listed in Table 1.

Beaver activity was evident near the lake's outlet and the water level seemed to be lowered about one meter from its original mark. Around the lake shore, the terrestrial vegetation was dominated by white pine, white and black spruce, white birch, cedar, and alder (Dickman in Fortescue et al. 1983). The littoral zone of the lake was minimal and most of the higher aquatic plants were confined to an area near the lake's outlet. The dominant plants were *Ledum* (labrador tea), *Vaccinium* (cranberry), and sedges.

B. *Lake CS* (85°53'W, 48°048'N)

Lake CS was classed as a soft water lake (conductivity 46 µmhos/cm). The lake occupied a small basin with a surface area of only 0.09 km^2 and drained a watershed of 1.8 km^2. At sampling site the maximum depth was 11 meters. The lake's bedrock geology was dominated by greenstone/granite (Fortescue et al. 1983). The surface water pH was 5.2 and the alkalinity was 1.56 mg/l as $CaCO_3$. The physical and chemical features are listed in Table 1.

The lake shore terrestrial vegetation was dominated by maple, white and yellow birch, mountain ash, poplar, and black and white spruce (Dickman in Fortescue et al. 1983). The littoral zone was minimal, and Ledum (labrador tea), Chamaedaphne (leather leaf), and small sedges were the major aquatic macrophytes present in the lake.

C. Lake U3 (Furnival Lake, 85° 56'W, 48° 13'N)

In comparison to Lake CS and Lake W1, Lake U3 had a larger surface (0.58 km^2) and watershed (4.25 km^2) area. The lakeshore bedrock geology was dominated by greenstone/granite. On the east shore of the lake, surficial deposits were predominant (Fortescue et al. 1983). The Secchi transparency was only 2.8 meters. The surface water pH was 7.05 and the alkalinity was 16.6 mg/l as $CaCO_3$. The maximum depth at the sampling site was 10 meters. The physical and chemical features of this lake are shown in Table 1.

The lake's shore line was complex and several rocky islands were visible in the lake. A few muskeg areas were also seen along the lake shore. In the watershed, the common terrestrial trees were black and white spruce, white birch, and cedar. The littoral zone was minimal and the common higher aquatic plants were Nuphar (yellow water lily), Nymphaea (white water lily), Potomogeton (pondweed), Equisetum (horse tail), and Vaccinium (cranberry) (Dickman in Fortescue et al. 1983).

D. Lake W1 (84°425'W, 48°05'N)

Lake W1 was located in the fume kill area. The bedrock geology was characterized by greenstone and a small portion of the watershed was covered by surficial deposits (Fortescue et al. 1983). The lake's surface area was small (0.02 km^2), and drained a relatively small watershed (0.19 km^2). The lake was the smallest of the four lakes chosen for my detailed study.

The surface water pH was 6.66 and the alkalinity was 13.26 mg/l as $CaCO_3$. The water was clear and the Secchi disk was visible on the bottom. The maximum depth at the sampling site was 2.3 meters. The chemical and physical features of this lake are shown in Table 1.

The watershed area was dominated by a large number of dead trees. The common trees were white and yellow birch, white and black spruce, maple, willow, pine, cedar, and poplar. The littoral zone was well developed. The common aquatic macrophytes were Typha (cattail), Nuphar (yellow water lily), Nymphaea (white water lily), Brasenia (water shield), Potamogeton (pondweed), Pontederia (pickerel weed), Sagittaria (arrowhead), Sparganium (bur reed), Scirpus (bulrush), Equisetum (horse tail), Carex (sedge), Ledum (labrador tea), and aquatic mosses. These macrophytes covered approximately, 15 to 20% of the shore line (Dickman in Fortescue et al. 1983).

MATERIALS AND METHODS

1. Core Sampling

During the field season, July 1981 and July 1982, 28 short sediment cores (circa 25-30 cm) were collected from 28 experimental lakes, north of Lake Superior, District Algoma, Ontario. The sediment cores were collected from or near the deepest point in the lakes using a K.B. gravity corer. The corer was equipped with a plexiglass coring tube (internal diameter 4.5 cm). The coring device was carefully lowered into the soft lake sediments to avoid the disturbance of core stratigraphy. The cores were carefully sealed in the field by using a plastic tape and brought back to the field base without disturbing the mud water interphase. In most of the cores the top centimeters were very soft and watery, while the rest of the sediment was homogenous and slightly more compact.

The sediment core extrusion was done as soon as possible (within 24 hours) at the field base by using a hydraulic extrusion system. The sediment cores collected in 1981 were sectioned at one centimeter intervals, but the 1982 sediment cores were sectioned at half centimeter intervals up to a depth of 5 cm and thereafter at one centimeter intervals. In order to maintain a consistancy in the surface sediments diatom analyses the homogenized top one centimeter sediment samples were used for all the 28 lakes. The extrusion system used in this study was found to be very useful for fine sectioning with a negligible amount of verical contamination in sediment samples. After the sectioning, the sediment samples were placed in prelabelled polythene whirl packs. The samples were stored in cold storage at 4°C and brought back to the Brock University laboratory for cleaning and preparing the permanent mounts.

2. Sediment Digestion and Diatom Preparation

An acid digestion technique was used for cleaning the diatoms. Small amounts of lake sediments (0.3 to 0.5 g) were taken in 100 ml beakers and 25 ml of concentrated sulfuric acid was added to each beaker. The beakers were heated to boiling under a fume hood for about 30 minutes. During the digestion, the samples were stirred using a spatula to avoid the accumulation of sediment on the bottom of the beakers. When the digestion of the organic matter was visually completed, the beakers were removed from the heating element and a small amount (0.3 to 0.5 g) of potassium dichromate was added to each beaker to oxidize any remaining organic matter. In each plastic vial a small amount of thymol (0.5 g) was added to avoid the fungal growth in samples.

After the digestion the samples were washed into centrifuge tubes with distilled water and centrifuged for two minutes at 6,000 rpm. The supernatant was carefully decanted and the pellet was resuspended in distilled water. This rinsing process was repeated three times to remove all the acid. After the final wash the diatoms were transferred to labelled plastic vials, and the distilled water was added to give a volume of 25 ml for each sample.

In all samples, the diatom concentrations were examined under the microscope and the samples were further diluted before placing them into the Battarbee plate (Battarbee 1973). The dilution was necessary to avoid the over crowding of diatom frustules in the final slides. The presence of too many frustules in the slide can cause considerable problems during their identification and counting.

In the each Battarbee plate 4 coverslips were positioned and a measured volume (generally 5 to 7 ml) of well mixed (homogenous) sample was poured into them. The plates were not disturbed after placing the samples. After 3 to 4 days, when all the water evaporated, the diatom coated coverslips were mounted on glass slides using Hyrax mounting media.

3. Diatom Identification and Counting

Diatom identification was based on Hustedt (1930), Huber-Pestalozzi (1942), Cleve-Euler (1951-1955), Nygaard (1956), Patrick and Reimer (1966, 1975), Gerloff and Cholnoky (1970), Foged (1979), Germain (1981), and Van Dam (1981).

For all samples, 800 or more diatom frustules were identified and enumerated in random strips under oil immersion (1,250 X magnification) using a "Leitz-Divert" inverted microscope equipped with Nomarski interference optics. For each sediment core, 20 samples or more were analyzed. A minimum of 5 coded replicate slides were also counted. Coding was necessary to avoid any unconscious bias. At selected levels, a third replicate slide was counted in order to obtain a standard deviation.

4. Diatoms and Assignment of pH Category

The diatoms were assigned a pH indicator value after a careful evaluation of 26 references selected from Beaver (1981). Although in the case of conflict the majority opinion was usually followed, substantial weight was given on the location of study area. Only with minor modifications, Hustedt's pH spectrum (1938) was used as a basic criterion for defining the pH limits of indicator groups. For the diatoms prefering a pH value around 7.0, the term indifferent was substituted by circumneutral and the indifferent pH category of this study included the diatoms which have no specific pH preferance and also the unidentified diatoms. All diatoms were grouped into the following 6 categories:

1. Acidobiontic : Occurring at a pH value under 7, optimum distribution at pH 5.5 or less.
2. Acidophilous : Occurring at a pH value about 7, widest distribution at pH below 7.
3. Circumneutral: Maximum occurrence on both sides of pH 7.
4. Alkaliphilous: Occurring at a pH value about 7, widest distribution at pH above 7.
5. Alkalibiontic: Occurring at a pH value above 7.
6. Indifferent : Diatoms do not have any specific pH preference or their pH information is unavailable in literature, and also the unidentified diatoms.

5. Calculation of Nygaard's Indices and the Construction of Calibration Curve

For the surface sediments of 28 study lakes, Nygaard's indices (1956) were used for calculating the index values. The following three indices were used for this purpose:

$$\text{Index alpha} = \frac{\text{acid units}}{\text{alkaline units}}$$

$$\text{Index omega} = \frac{\text{acid units}}{\text{number of acid taxa}}$$

$$\text{Index epsilon} = \frac{\text{alkaline units}}{\text{number of alkaline taxa}}$$

where as:

Acid units = Relative frequency of acidophilous taxa + relative frequency of acidobiontic taxa X 5.

Alkaline units = Relative frequency of alkaliphilous taxa + relative frequency of alkalibiontic taxa X 5.

In order to prepare a calibration curve for calculating the downcore pH patterns, the index alpha, omega, and epsilon results were transformed to log scale and plotted against the observed lake pH. The details of these curves will be discussed in the results and discussion sections.

6. <u>Downcore Diatom Inferred pH</u>

The index alpha regression equation was used to construct the downcore paleo-pH profiles of lakes X4, CS, U3, and W1.

7. <u>Sediment Core Dating</u>

Three major dating techniques; Ambrosia horizon, Cesium-137, and Lead-210 were used for obtaining the various markers in the sediment cores.

a. <u>Ambrosia</u>: <u>Ambrosia</u> analyses were provided by Dr. J. Terasmae, Department of Geological Sciences, Brock University. In sediment cores, the <u>Ambrosia</u> horizon marked a period around 1890 when the settlers moved in the Great Lake region. This information was available for all the lakes (CS, X4, U3, and W1).

b. Cs-137: This information was provided by Dr. M.D. Dickman. The Cs-137 dating marked a period between 1950 and 1960 when the Cs-137 concentrations increased in the sediments due to the open air atomic bomb testing (Norton et al. 1981). CS-137 marks were available for CS, X4, and U3 lakes.

c. Lead-210: The Lead-210 dates were only available for Lake W1. This information was also provided by Dr. M.D. Dickman.

8. Limnological Investigation

The following limnological details were collected in the field:

a. pH: The surface water pH of all 28 lakes was measured at the site, using a Metrohm Herisau (model E 488) pH meter. The meter was calibrated by using pH 4 and 7 buffer solutions.

b. Conductivity: The surface water conductivity (µmhos/cm) of all the 28 lakes was measured by using a YS1 (model 33) conductivity meter.

d. Photic zone: For all the study lakes, the water column transparency was determined using a Secchi disk.

e. Other chemical features such as alkalinity, calcium, sulphate, and colour were adopted from Fortescue et al. (1983).

RESULTS

1. Surface Sediment Diatom Analysis

The surface sediment diatoms (0-1 cm) of 28 study lakes were analyzed in detail. A total of 181 diatom taxa were encountered in the surface sediments of these lakes. The detailed listing of these diatoms and their pH indicator status are shown in Table 2.

A. Surface sediment diatoms of acidic lakes (pH <5.6)

Among the 28 study lakes, thirteen lakes (X1, X2, X3, X4, Z1, Z2, Z3, Z4, CS, CB1, CB2, B, and CF) had an observed pH value below 5.6. In these lakes the surface water pH ranged from a low of 4.40 to a high of 5.48, and the alkalinity from a low of -0.51 mg/l as $CaCO_3$ to a high of 5.38 mg/l as $CaCO_3$ (Table 1).

In acidic lakes, the acidophilous diatom population was most abundant (Fig.4). Their population size ranged between 30% (CS Lake) to 73% (X2 Lake) of the total diatom population. In acidic lakes the common acidophilous diatom taxa (ie. those greater than 2% of the total diatom population) were *Anomoeoneis serians* var. *brachysira*, *Eunotia bidentula*, *E. gibbosa*, *E. pectinalis*, *E. pectinalis* var. *ventricosa*, *E. flexuosa*, *Frustulia rhomboides*, *Melosira distans*, *Pinnularia biceps*, *P. abaujensis* var. *rostrata*, *Tabellaria fenestrata*, *T. flocculosa*, and *Stenopterobia intermedia*.

The acidobiontic diatoms were not as abundant as the acidophilous diatoms in the acidic lakes (Fig.4). Their population size ranged between 5% (Lake CS) and 19% (Lake X1) of the total diatom population.

Table 2. List of diatom taxa identified in the suface sediments of 28 study lakes. alp = alkaliphilous, cir = circumneutral, acp = acidophilous, acb = acidobiontic, ind = indifferent, "-" = pH indicator status unknown.

Achnanthes Bory	
affinis Grun.	alp
deflexa Reim.	alp
exigua Grun.	alp
flexella (Kutz.) Brun.	ind
lacunarum Hust.	-
lanceolata (Breb.) Grun.	alp
linearis (W. Sm.) Grun.	alp
minutissima Kutz.	cir
Actinella Lewis	
punctata Lewis	acb
Amphora Ehr. ex Kutz.	
ovalis Kutz.	alp
Anomoeoneis Pfitz.	
follis (Ehr.) Cl.	cir
serians var. brachysira (Breb. ex Kutz.) Hust.	acp
serians (Breb. ex Kutz.) cl.	acb
vitrea (Grun.) Ross.	alp
zellensis (Grun.) Cl.	-
Asterionella Hass.	
formosa Hass	ind
Caloneis Cl.	
ventricosa (Ehr.) Meist.	alp
Cocconeis Ehr.	
placentula Ehr.	alp
pediculus Ehr.	alp
Cyclotella Kutz..	
bodanica Eulenst.	alp
comta (Ehr.) Kutz.	cir
meneghiniana Kutz.	alp
stelligera (Cl.& Grun.) V.H.	alp
Cymatopleura Breb.	
solea (Breb.) W. Sm.	-
Cymbella Ag.	
amphicephala Naeg. ex Kutz.	ind
angustata (W. Sm.) Cl.	alp
cesatii (Rabh.) Grun. ex A.S.	cir
cistula (Ehr.) Kirchn.	alp

Table 2 (continued)

Cymbella Ag.	
cuspidata Kutz.	alp
cymbioformis Ag.	ind
delicatula Kutz.	ind
hauckii V. Heurck.	alp
helvetica Kutz.	alp
hustedtii Krasske.	-
lunata W. Sm.	cir
microcephala Grun.	cir
minuta Hilse ex Rabh.	cir
muelleri Hust.	alp
pusilla Grun.	acp
sp.	-
Denticula Kutz.	
elegans f. valida Pedic.	alp
sp.	-
Diploneis Ehr.	
finnica (Ehr.) Cl.	cir
marginestriata Hust.	alp
oculata (Breb.) Cl.	ind
smithi (Breb. ex. W. Sm.) Cl.	cir
Epithemia Breb.	
adnata (Kutz.) Breb.	alp
argus var. alpestris Grun.	alp
sp.	
Eunotia Ehr.	
arcus Ehr.	acp
bactriana Ehr.	acb
bidentula W. Sm.	acp
bigibba Kutz.	acp
carolina Patr.	acp
curvata (Kutz.) Lager.	acp
elegans Oster.	acp
exigua (Breb. ex Kutz.) Rabh.	acb
flexuosa Breb. ex Kutz.	acp
gibbosa Grun.	acp
glacilis Meist.	acp
hexaglyphis Ehr.	acp
incisa W. Sm. ex Greg.	acp
meisteri Hust.	acp
monodon Ehr.	acp
naegelli Migula.	acp
pectinalis var. minor (Kutz.) Rabh.	acp
pectinalis (O. Mull.) Rabh.	acp
pectinalis var. ventricosa Grun.	acp
praerupta Ehr.	acp
rostellata Hust. ex Patr.	acp
septentrionalis Ostr.	acp

Table 2 (continued)

Eunotia Ehr.	
serra Ehr.	acp
triodon Ehr.	acp
valida Hust.	acp
vanheurckii Patr.	acp
Fragilaria Lyngb.	
brevistriata Grun.	alp
constricta Ehr.	acp
construens var. binodis (Ehr.) Grun.	ind
construens (Ehr.) Grun.	alp
construens var. venter (Ehr.) Grun.	alp
crotonensis Kitton.	alp
lapponica Grun.	ind
leptostauron var. dubia. (Grun.) Hust.	alp
pinnata var. intercedens (Grun.) Hust.	alp
pinnata Ehr.	alp
vaucheriae (Kutz.) Peter.	alp
virescens Ralf.	cir
Frustulia Rabh.	
rhomboides var. capitata (A. Mayer) Patr.	acp
rhomboides (Ehr.) DeT.	acp
rhomboides var. saxonica Hust.	acp
vulgaris (Thw.) DeT.	ind
Gomphonema Ehr.	
acuminatum Ehr.	alp
angustatum Ehr.	alp
clevi Fricke.	ind
grunowii Patr.	-
intricatum Kutz.	alp
subtile Ehr.	acp
truncatum Ehr.	alp
Melosira Ag.	
distans (Ehr.) Kutz.	acp
granulata (Ehr.) Ralfs	alp
italica (Ehr.) Ralfs	ind
italica subsp. subarctica O. Mull.	alp
Navicula Bory	
aurora Sov.	alp
bacillum Ehr.	alp
bicephala Hust.	-
capitata Ehr.	alp
cryptocephala Kutz.	ind
cuspidata (Kutz.) Kutz.	alp
elginensis (Greg.) Ralfs	alp
elginensis var. rostrata (A. Mayer) Patr.	-

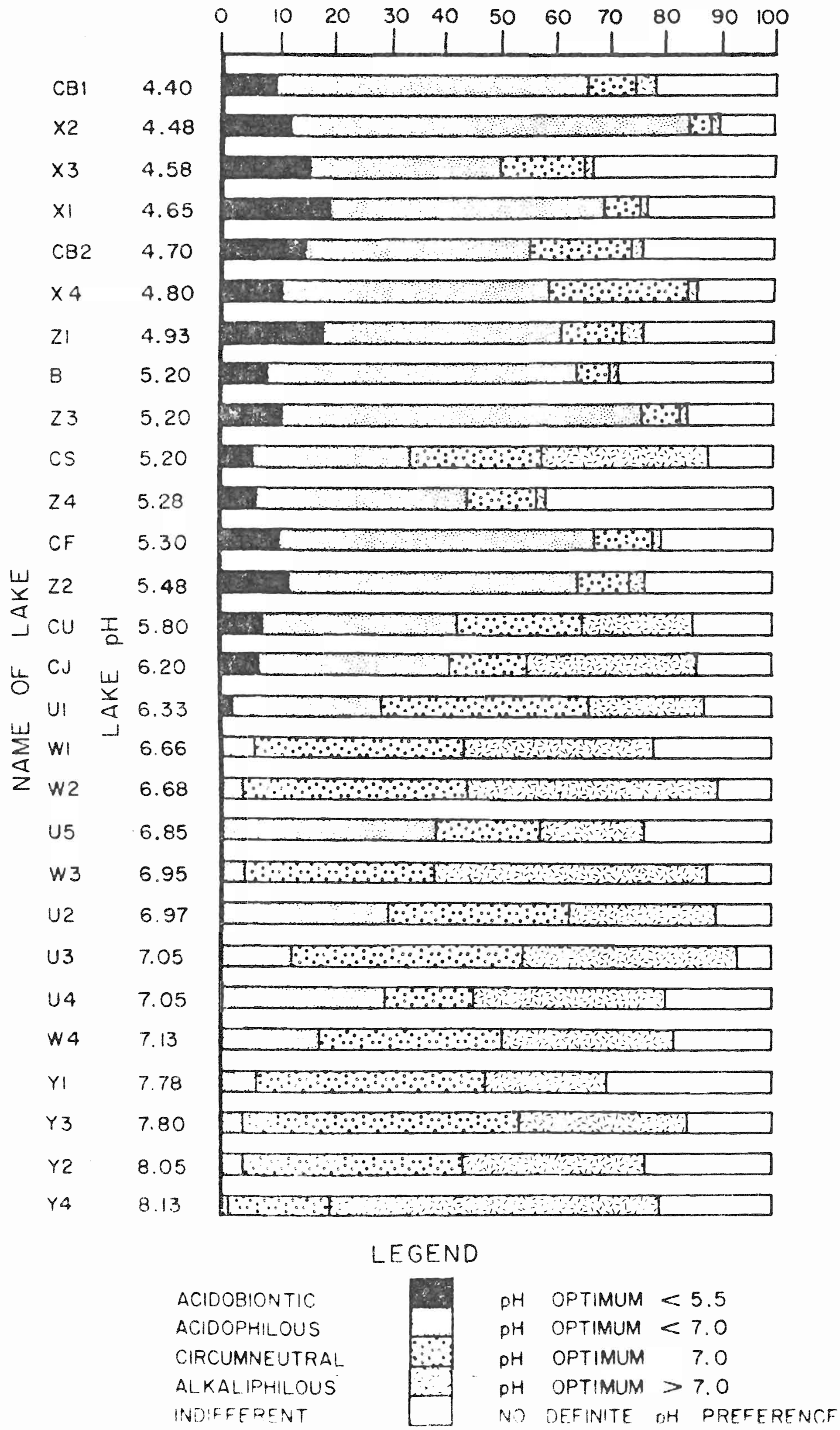
Table 2 (continued)

Navicula Bory	
gottlandica Grun.	cir
hustedtii Krasske	ind
lanceolata (Ag.) Kutz.	alp
minima Grun.	alp
notha Wallace	-
peregrina (Ehr.) Kutz.	cir
pupula var. capitata Skv.& Mayer	cir
pupula Kutz.	cir
pupula var. rectangularis (Greg.) Grun.	cir
radiosa var. parva Wallace	cir
radiosa Kutz.	cir
radiosa var. tenella (Breb. ex Kutz.) Grun.	cir
subtillissima Cl.	ind
tripunctata (V.H.) Patr.	alp
viridula (Kutz.) Kutz. emend. V.H.	alp
vulpina Kutz.	ind
sp.	
Nedium Pfitz.	
affine (Ehr.) Pfitz.	ind
bisulcatum (Lager) Cl.	ind
hitchcockii (Ehr.) Cl.	acp
iridis var. amphigomphus (Ehr.) A. Mayer	ind
iridis (Ehr.) Cl.	cir
Nitzschia Hass.	
acicularis W. Sm.	alp
amphibia Grun.	alp
denticula Grun.	alp
denticula var. curta Grun.	alp
fonticola Grun.	alp
hantzschiana Rabh.	cir
intermedia Hantzsch.	alp
kutzingiana Hilse.	alp
linearis W. Sm.	alp
palea (Kutz.) W. Sm.	cir
sinuata (W. Sm.) Grun.	cir
Pinnularia Ehr.	
abaujensis (Pant.) Ross	ind
abaujensis var. linearis (Hust.) Patr.	ind
abaujensis var. rostrata (Patr.) Patr.	acp
acuminata var. biewlowskii (Herib. & Perag.) Patr.	alp
biceps Greg.	acp
brebissonii (Kutz.) Rabh.	cir
divergens W. Sm.	acp
formica (Ehr.) Patr.	-
hilseana Jan.	-
maior (Kutz.) Rabh.	ind
mesolepta (Ehr.) W. Sm.	acp
microstauron (Ehr.) Cl.	acp

Table 2 (continued)

Pinnularia Ehr.	
nodosa (Ehr.) W. Sm.	acp
rupestris Hantz	-
subcapitata Greg.	cir
substomatophora Hust.	-
viridis (Nitz.) Ehr.	cir
Rhopalodia O. Mull.	
gibba (Ehr.) O. Mull.	alp
parallela (Grun.) O. Mull.	alp
Semiorbis Patr.	
hemicyclus (Ehr.) Patr.	acb
Stauroneis Ehr.	
acuta W. Sm.	alp
anceps Ehr.	cir
livingstonii Reim.	-
phoenicenteron (Nitz.) Ehr.	cir
Stenopterobia Lewis	
intermedia Lewis	acp
Surirella Turpin	
delicatissima Lewis	ind
linearis var. constricta (Ehr.) Grun.	ind
linearis W. Sm.	ind
robusta Ehr.	ind
Synedra Ehr.	
acus Kutz.	cir
delicatissima W. Sm.	cir
parasitica (W. Sm.) Hust.	alp
radians Kutz.	alp
ulna (Nitz.) Ehr.	alp
sp.	-
Tabellaria Ehr.	
binalis (Ehr.) Grun.	acb
fenestrata (Lyngb.) Kutz.	acp
flocculosa (Roth) Kutz.	acp

Figure 4. The percent composition of pH indicator and pH indifferent diatoms from the surface sediments (0-1 cm) of 28 study lakes.


0 10 20 30 40 50 60 70 80 90 100
NAME OF LAKE
LAKE pH
CB1 4.40
X2 4.48
X3 4.58
X1 4.65
CB2 4.70
X4 4.80
Z1 4.93
B 5.20
Z3 5.20
CS 5.20
Z4 5.28
CF 5.30
Z2 5.48
CU 5.80
CJ 6.20
U1 6.33
W1 6.66
W2 6.68
U5 6.85
W3 6.95
U2 6.97
U3 7.05
U4 7.05
W4 7.13
Y1 7.78
Y3 7.80
Y2 8.05
Y4 8.13
LEGEND
ACIDOBIONTIC pH OPTIMUM < 5.5
ACIDOPHILOUS pH OPTIMUM < 7.0
CIRCUMNEUTRAL pH OPTIMUM 7.0
ALKALIPHILOUS pH OPTIMUM > 7.0
INDIFFERENT NO DEFINITE pH PREFERENCE

With the exception of Lake Z2 (pH 5.48), the acidobiontic diatom population was higher in the acidic lakes of pH value below 5.2 (Z1, X4, CB2, X1, X3, X2, and CB1) than the lakes of higher pH (B, Z3, CS, Z4, and CF). The identified acidobiontic taxa were Actinella punctata, Anomoeoneis serians, Eunotia exigua, E. bactriana, Semiorbis hemicyclus, and Tabellaria binalis. All these acidobiontic taxa were common and contributed more than 2% of the total diatom population.

The circumneutral diatom population fluctuated between 4% (X2 Lake) and 29% (X4 Lake) of the total (Fig.4). No definite pattern existed in the distribution of circumneutral diatoms. The common circumneutral taxa were Cyclotella comta, Cymbella minuta, Nedium iridis, Stauroneis anceps, and S. phoenicenteron.

Except for Lake CS, the alkaliphilous diatom population was extremely low in the acidic lakes (0.5 - 4.0% of the total diatom population, Fig.4). In Lake CS, the alkaliphilous diatoms accounted for an unusually high percentage (33%). In the surface sediment of Lake CS, the common alkaliphilous forms were Cyclotella meneghiniana, Fragilaria construens, and F. crotonensis. In other acidic lakes the population size of individual alkaliphilous diatom species was always less than 2% of the total.

The distribution of pH indifferent diatoms ranged between 10 to 41% of the total diatom population (Fig.4). In Lake X4, their extreme abundance (41%) was primarily due to the higher numbers of Frustulia vulgaris. Although the unidentified diatoms were also included in the pH indifferent category of Fig.4, their abundance was always less than 2% of the total diatom population.

In acidic lakes, the number of diatom taxa ranged between 38 and 59 (Fig.5). The maximum number of diatom taxa were observed in Lake Z2. Among all the acidic lakes this lake had the maximum observed pH (pH 5.48). The number of diatom taxa observed in the acidic lakes were lower than those in the slightly acidic, neutral, or alkaline lakes (Fig.5). In most of the acidic lakes the acidophilous diatom taxa accounted for almost 50% of the total species richness. The number of acidobiontic and circumneutral diatom taxa ranged between 4-6 and 5-11 respectively. Excluding Lake CS, only 2-5 alkaliphilous diatom taxa were seen in the acidic lakes. Lake CS behaved rather strangely in this respect with 10 alkaliphilous diatom taxa. The reasons for this will be discussed in the following section (discussion).

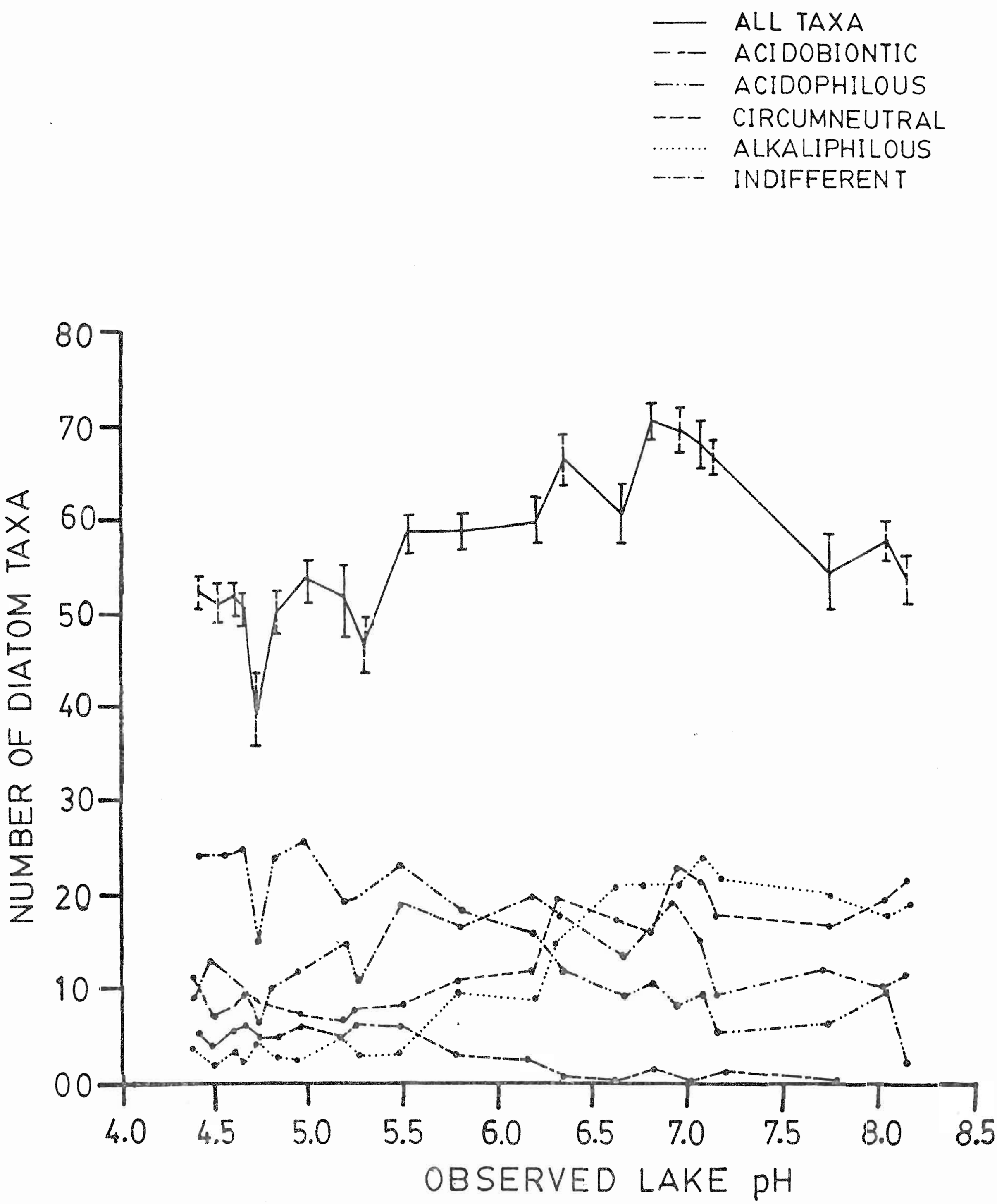
B. Surface sediment diatoms of slightly acidic lakes (pH 5.6 - 6.5)

The CU, CJ, and U1 lakes fell into this pH category. For these lakes the surface water pH results were 5.80, 6.20, and 6.33 and the alkalinity was 0.40, 3.69, and 8.75 mg/l as $CaCO_3$ respectively.

Similar to acidic lakes, the acidophilous diatoms were most abundant in the slightly acidic lakes (Fig.4). However, their population was lower and it gradually declined (39-28%) as the lake's pH increased from CU to U1 Lake (pH 5.80-6.33). The common acidophilous diatoms were *Anomoeoneis serians* var. *brachysira*, *Frustulia rhomboides*, *Pinnularia biceps*, *Tabellaria fenestrata*, and *T. flocculosa*.

Acidobiontic diatoms were also present in the surface sediments of slightly acidic lakes, but their dominance was less (2-7%) than that

Figure 5. Surface sediment diatom species richness as a function of lake pH. Solid horizontal bars represent standard deviations about the mean (n=3) and broken horizontal bars represent ranges for two counts.



ALL TAXA
ACIDOBIONTIC
ACIDOPHILOUS
CIRCUMNEUTRAL
ALKALIPHILOUS
INDIFFERENT
NUMBER OF DIATOM TAXA
80
70
60
50
40
30
20
10
00
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
OBSERVED LAKE pH

observed in the acidic lakes (5-19%). The only acidobiontic diatoms observed were Actinella punctata, Anomoeoneis serians, Eunotia exigua, and Semiorbis hemicyclus.

In slightly acidic lakes, the circumneutral and alkaliphilous diatoms contributed 14-39% and 19-34% of the total diatom population (Fig.4). The common circumneutral diatom taxa were Cymbella cesatii, C. minuta, Fragilaria virescens, Navicula radiosa var. parva, N. pupula var. rectangularis, Nedium iridis, Achnanthes minutissima, and Stauroneis phoenicenteron. The alkaliphilous diatom population was dominated by Anomoeoneis vitrea, Cyclotella meneghiniana, Cymbella angustata, and Nitzschia fonticola. In the slightly acidic lakes, the pH indifferent diatoms contributed only 12 to 15% of the total diatom population.

In the slightly acidic lakes, the diatom species richness was higher than the acidic lakes (Fig.5). As lake pH increased, the number of diatom taxa gradually increased from a low of 59 in Lake CU to a high of 67 in Lake U1. The acidophilous and pH indifferent diatom taxa were the major contributers to the species richness. There was also an inverse relationship between the number of acidophilous and alkaliphilous diatom taxa; ie. with the increase in pH the number of acidophilous diatom taxa decreased (18-13) and the number of alkaliphilous taxa increased (10-16). In these lakes the number of acidobiontic taxa (1-3) were also lower than the acidic lakes (4-6). Very similar to alkaliphilous forms, the number of circumneutral diatom taxa increased (11-19) as the lake pH increased, but the number of pH indifferent diatom taxa remained very constant (17-20, Fig.5).

C. <u>Surface sediment diatoms of circumneutral lakes (pH 6.6 - 7.5)</u>

Eight of the 28 study lakes were in this pH category. These lakes were W1, W2, W3, W4, U2, U3, U4, and U5. The surface water pH and alkalinity results of these lakes ranged between pH 6.66 - 7.13 and 13.26 - 18.25 mg/l as $CaCO_3$ (Table 1).

In circumneutral lakes, the acidobiontic diatom population was very sparse (<1% of the total diatom population, Fig.4). Only two acidobiontic taxa, <u>Actinella punctata</u> and <u>Anomoeoneis serians</u> were observed in these lakes. In comparison to acidic and slightly acidic lakes, the acidophilous diatom population was also significantly lower in the circumneutral lakes. The acidophilous diatom population greatly fluctuated between U (U2, U3, U4, U5) and W series lakes (W1, W2, W3, W4). In the U lakes, the acidophilous diatoms were far more abundant (28 to 37%) than in the W lakes (4 to 18%). The common acidophilous diatom taxa were <u>Anomoeoneis serians</u> var. <u>brachysira</u>, <u>Tabellaria fenestrata</u>, <u>T. flocculosa</u>, and <u>Melosira distans</u>.

The circumneutral diatom population remained relatively uniform in all but lakes U4 and U5 (Fig.4). The common circumneutral taxa were <u>Achnanthes minutissima</u>, <u>A. flexella</u>, <u>Cymbella cesatii</u>, <u>C. minuta</u>, <u>Navicula radiosa</u> var. <u>parva</u>, <u>N. pupula</u> var. <u>rectangularis</u>, <u>Stauroneis phoenicenteron</u>, and <u>Synedra radians</u>.

The alkaliphilous diatom population was most abundant in the circumneutral lakes with the exception of Lake U5 (Fig.4). Their population size ranged between 18 and 47% of the total. The common alkaliphilous diatoms were <u>Achnanthes affines</u>, <u>A. linearis</u>, Anomoeoneis vitrea, Cyclotella bodanica, C. meneghiniana, Cymbella helvetica, C. angustata, Fragilaria construens, F. pinnata, Nitzschia fonticola, N. denticula, and Melosira granulata. The pH indifferent diatoms represented 7 to 24% of the total diatom population (Fig.4).

The number of diatom taxa observed in circumneutral lakes was higher than for acidic or alkaline lakes (Fig.5). A range of 55 to 71 diatom taxa were encountered in these lakes. In circumneutral lakes, the number of acidobiontic (0-1) and acidophilous diatom taxa (5-14) significantly declined and the number of circumneutral (16-26) and alkaliphilous (21-24) diatom taxa significantly increased. The number of pH indifferent diatom taxa ranged between 13 and 19.

D. Surface sediment diatoms of alkaline lakes (pH > 7.5)

Among the 28 study lakes, only the Y series lakes (Y1, Y2, Y3, Y4) were alkaline. In these lakes the surface water pH ranged between 7.78 - 8.13 and the alkalinity results ranged from 84.5 to 108.5 mg/l as $CaCO_3$ (Table 1).

In these alkaline lakes, the acidobiontic diatoms were absent and the abundance of acidophilous diatoms was extremely low (only 1 to 6% of the total diatom population, Fig.4). Anomoeoneis serians var. brachysira, Frustulia rhomboides, Pinnularia biceps, P. abaujensis var. rostrata, Tabellaria fenestrata, and T. flocculosa were the only acidophilous diatoms of alkaline lakes. The percent composition of these individual diatom species was always less than 2% of the total diatom population.

The circumneutral diatoms were most abundant in Y1, Y2, and Y3 lakes and they accounted for 42, 40, and 50% of the total diatom population respectively (Fig.4). In Lake Y4 the circumneutral diatom population was very low (19%). The common circumneutral diatom taxa were Achnanthes minutissima, Cyclotella comta, Cymbella cesatii, C. minuta, Navicula radiosa var. parva, and N. pupula var. rectangularis.

In the 4 alkaline lakes, the alkaliphilous diatoms contributed a significant portion of the total diatom population and their abundance gradually increased as lake pH increased (23-58%, Fig.4). The common alkaliphilous diatom taxa were Achnanthes exigua, A. lanceolata, Amphora ovalis, Anomoeoneis vitrea, Cyclotell meneghiniana, Cymbella angustata, Fragilaria construens, F. construens var. venter, F. pinnata, and Nitzschia fonticola. As noted in the other study lakes, the pH indifferent diatom population of these lakes did not have any definite distribution pattern (Fig.4).

In the 4 alkaline lakes, the diatom species richness (54-58) was lower than for the neutral pH lakes (Fig.5). The majority of diatom taxa were associated with circumneutral (17-22) and alkaliphilous (18-20) pH indicator groups. The acidobiontic diatom taxa were absent in the alkaline lakes and the number of acidophilous diatom taxa were considerably lower (6-10) than the acidic (16-26) and slightly acidic lakes (13-18). The number of pH indifferent diatom taxa (10-15) did not vary appreciably from lake to lake.

2. Major pH Indicator Diatoms and Observed Lake pH

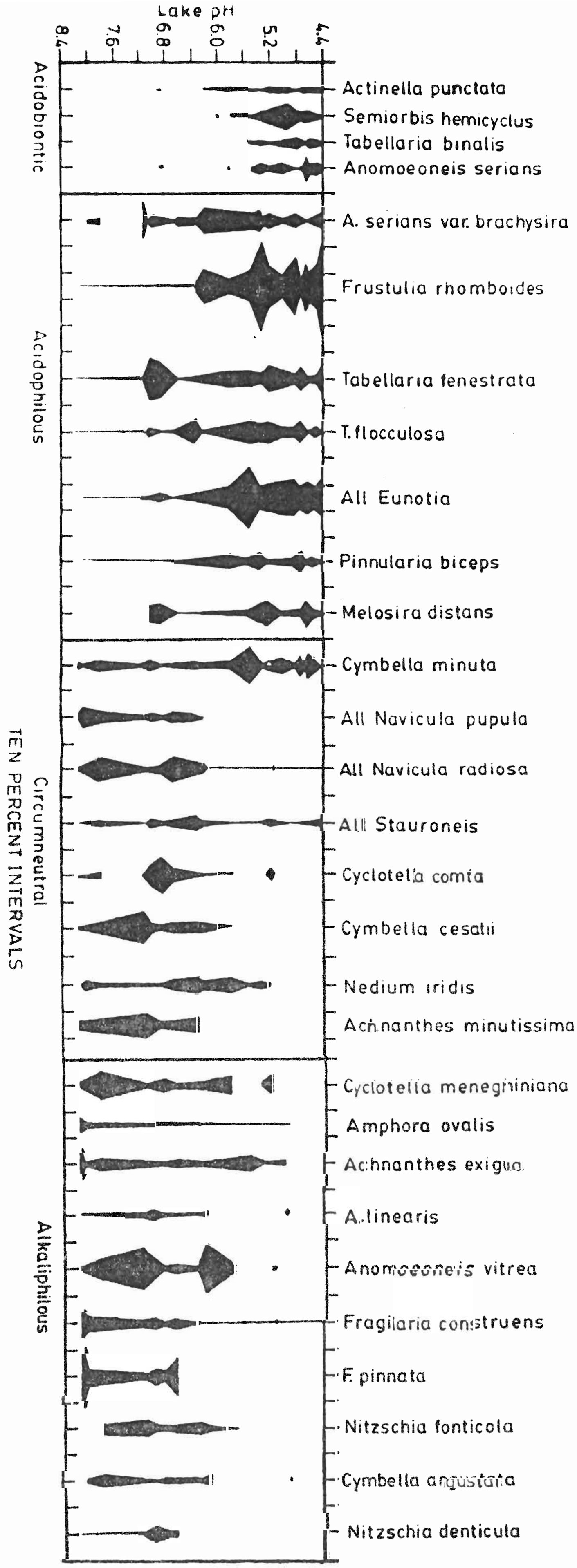
The distribution of 29 major pH indicator diatoms of the surface sediments of 28 study lakes is shown in Fig.6. These pH indicator diatoms comprised a minimum of 3% of the total diatom population. As discussed in the methods section, the assignment of pH category was based entirely on the critical evaluation of 26 selected references from Beaver (1981).

Four major acidobiontic diatom taxa (*Actinella punctata*, *Semiorbis hemicyclus*, *Tabellaria binalis*, and *Anomoeoneis serians*) predominated in the low pH lakes. *Semiorbis hemicyclus*, *Tabellaria binalis*, and *Anomoeoneis serians* appear to prefer more acidic conditions than *Actinella punctata* (Fig.6).

In general, the population of individual acidophilous diatom taxa was higher in lakes with pH values below 6.4 (Fig.6). However, *Anomoeoneis serians* var. *brachysira* and *Tabellaria fenestrata* represented an unusual maximum around pH 7. The other acidophilous diatoms (*Frustulia rhomboides*, *Tabellaria flocculosa*, *Eunotia* spp., *Pinnularia biceps*, and *Melosira distans*) displayed their maximum population between pH 5.2 and 5.6.

Among the eight common circumneutral diatom taxa, only *Cyclotella comta*, *Cymbella cesatii*, *Achnanthes minutissima*, and *Stauroneis* spp. (*S. phoenicenteron* and *S. anceps*) peaked in abundance in the neutral pH waters. The abundance of *Navicula radiosa* was higher in

Figure 6. The relative abundance of 29 major pH indicator diatoms of 28 study lakes distributed as a function of lake pH.



Lake pH
8.4
7.6
6.8
6.0
5.2
4.4
Acidobiontic
Actinella punctata
Semiorbis hemicyclus
Tabellaria binalis
Anomoeoneis serians
Acidophilous
A. serians var. brachysira
Frustulia rhomboides
Tabellaria fenestrata
T. flocculosa
All Eunotia
Pinnularia biceps
Melosira distans
Circumneutral
TEN PERCENT INTERVALS
Cymbella minuta
All Navicula pupula
All Navicula radiosa
All Stauroneis
Cyclotella comta
Cymbella cesatii
Nedium iridis
Achnanthes minutissima
Alkaliphilous
Cyclotella meneghiniana
Amphora ovalis
Achnanthes exigua
A. linearis
Anomoeoneis vitrea
Fragilaria construens
F. pinnata
Nitzschia fonticola
Cymbella angustata
Nitzschia denticula

circumneutral as well as in alkaline lakes, and *Navicula pupula*, demonstrated slightly higher populations in alkaline lakes. The populations of the remaining two circumneutal diatoms, *Cymbella minuta* and *Nedium iridis* were highest under acidic conditions.

Ten major alkaliphilous diatom taxa were seen in the surface sediments of the 28 study lakes (Fig.6). Among them, *Cyclotella meneghiniana*, *Amphora ovalis*, *Achnanthes exigua*, *Fragilaria construens*, *F. pinnata*, *Nitzschia fonticola*, and *Cymbella angustata* demonstrated higher populations in alkaline waters. However, *Nitzschia denticula* and *Achnanthes linearis* expressed their optimum dominance in circumneutral lakes. Contrary to expectation, *Anomoeoneis vitrea* was present in alkaline as well as in the slightly acidic environment.

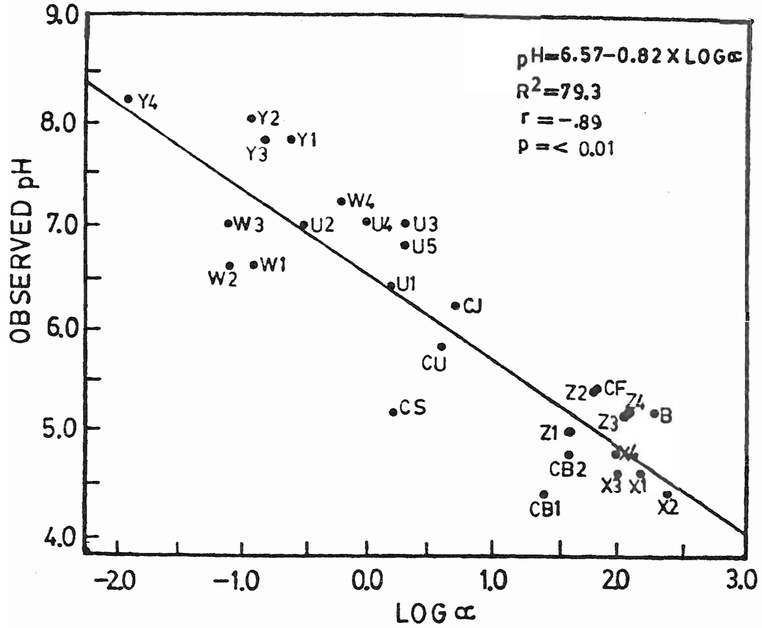
3. Calibration Curve

Three different approaches were considered in constructing the calibration curve. This was done by the use of Nygaard's (1956) index alpha, index omega, and index epsilon. According to their optimum pH preference, the surface sediment diatoms of 28 lakes were classified into Hustedt's pH spectra (1938) and the relative abundance of the individual pH indicator group was calculated (Fig.4). Later Nygaard's indices were transformed to log scale and plotted against the observed lake pH (Fig.7).

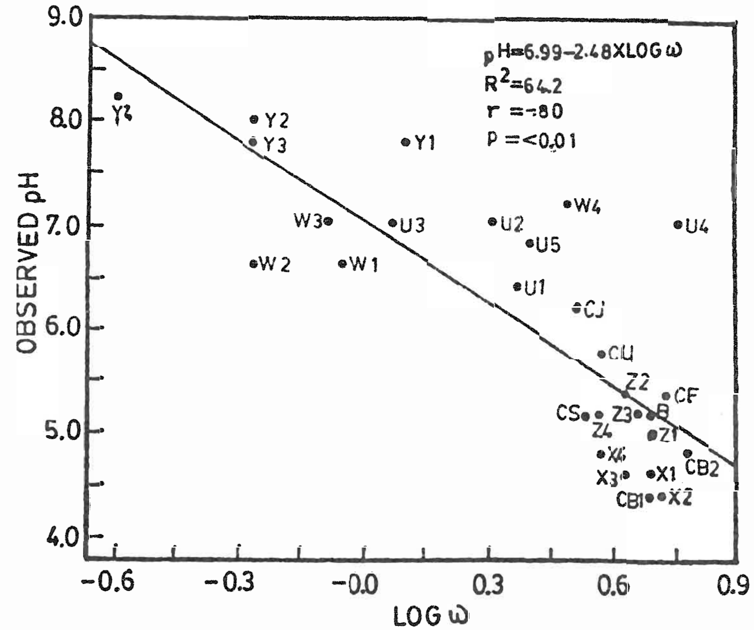
A linear relationship was observed between the index log alpha (ratio of acid and alkaline units) and that of observed lake pH

Figure 7. The relationship between Nygaard's indices and observed lake pH for 28 study lakes, A. log index alpha; B. log index omega; C. log index epsilon.

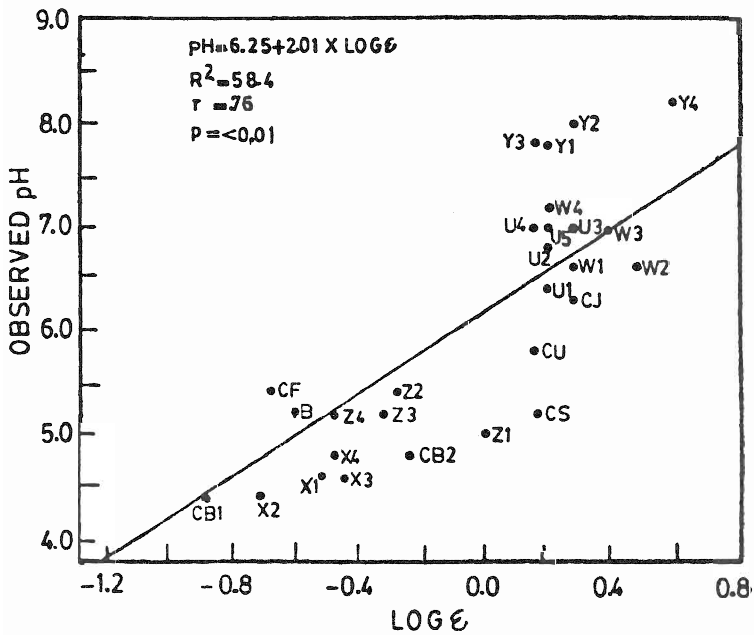
(A)


pH=6.57−0.82 X LOGα
R^2=79.3
r =−.89
P =< 0.01
OBSERVED pH
LOG α

(B)


pH=6.99−2.48XLOG ω
R^2=64.2
r =−.80
P =<0.01
OBSERVED pH
LOG ω

(C)


pH=6.25+2.01 X LOG ε
R^2=58.4
r =.76
P =<0.01
OBSERVED pH
LOG ε

(Fig.7A). The relationship was highly significant ($r=-0.89$; $p=<0.01$) and 80% of variance in the diatom inferred pH was explained by the regression line. The index omega regression (Fig.7B), which is a measure of mean relative frequency of the acidic taxa was similar to the index alpha regression, but the relationship was not as strong ($r=-0.80$; $p=<0.01$) and only 64% of the variance was explained by the regression line. Moreover, in the index omega regression line, most of the low pH lakes fell below the regression line while the majority of neutral and alkaline lakes fell above the regression line. The index epsilon, which is a measure of mean relative frequency of alkaline taxa, displayed a positive relationship between the index log epsilon and observed lake pH (Fig.7C). The relationship was also significant for the index epsilon ($r= 0.76$; $p=<0.01$), but only 58% of the variance was explained by the regression line.

The index alpha diatom inferred and observed lake pH results were both in good agreement (Table 3). Out of the 28 lakes, ten (36%) had diatom inferred pH within 0.3 of a pH unit and twelve (43%) were within 0.3 to 0.6 of a pH unit from the observed pH. Four lakes (14%) were within 0.6 to 1.0 pH unit of the observed pH and the 2 remaining lakes had a difference of more than 1 pH unit (1-1.3 pH unit). In comparison to index alpha, the index omega and index epsilon diatom inferred pH results lacked the precision of index alpha (Table 3).

Table 3. The relationship between diatom inferred and observed lake pH.

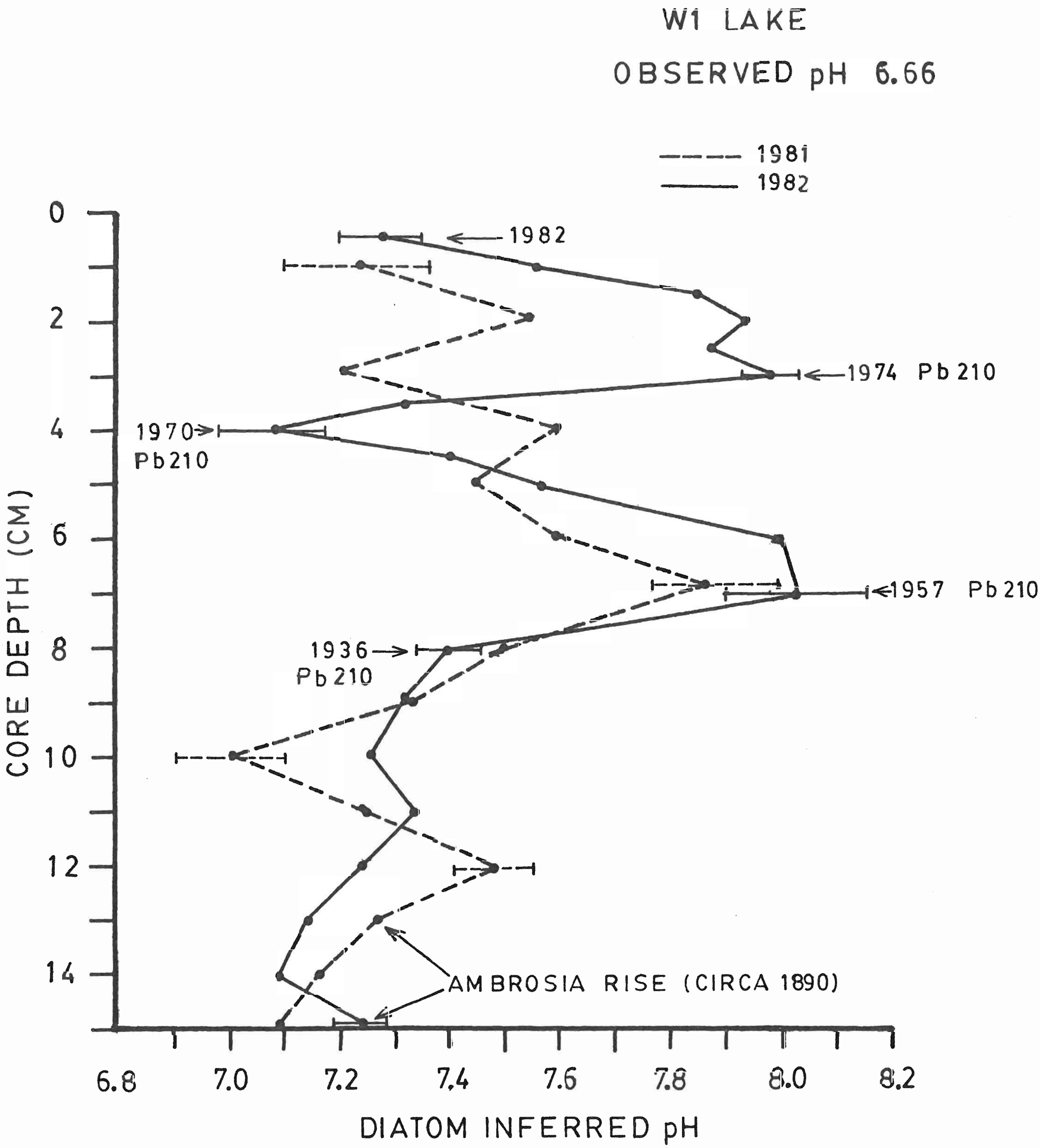
Lake	Observed pH	Diatom inferred pH Index alpha	Index omega	Index epsilon
CB 1	4.40	5.46	5.25	4.46
X 2	4.48	4.61	5.23	4.80
X 3	4.58	4.90	5.45	5.33
X 1	4.65	4.76	5.28	5.20
CB 2	4.70	5.30	5.08	5.75
X 4	4.80	4.92	5.58	5.27
Z 1	4.93	5.30	5.30	6.20
B	5.20	4.70	5.25	5.04
Z 3	5.20	4.86	5.35	5.62
CS	5.20	6.46	5.55	6.59
Z4	5.28	4.86	5.63	5.31
CF	5.30	5.13	5.20	4.88
Z 2	5.48	5.10	5.43	5.65
CU	5.80	6.12	5.58	6.57
CJ	6.20	6.01	5.70	6.77
U 1	6.33	6.40	6.10	6.67
W 1	6.66	7.28	7.11	6.83
W 2	6.68	7.47	7.68	7.23
U 5	6.85	6.83	6.02	6.67
W 3	6.95	7.46	7.21	7.01
U 2	6.97	6.59	6.25	6.67
U 3	7.05	7.02	6.84	6.81
U 4	7.05	6.82	5.15	6.57
W 4	7.13	6.76	5.80	6.67
Y 1	7.78	7.03	6.74	6.63
Y 3	7.80	7.27	7.66	6.59
Y 2	8.05	7.30	7.66	7.79
Y 4	8.13	8.13	8.47	7.44

4. Repeatability of Paleo-pH Technique

In order to determine the repeatability of downcore diatom inferred pH, two paleo-pH profiles of Lake W1 were made (Fig.8). These pH profiles were constructed from independent diatom analysis of 2 sediment cores obtained from 2 different sites in Lake W1. The 1982 paleo-pH profile was the one which was used here to study the detailed pH history of Lake W1. The 1981 paleo-pH profile was generated from another sediment core collected during the 1981 field season. The diatom counts of the 1981 sediment core were provided by Mr. Kit Yung.

The 1981 and 1982 paleo-pH profiles displayed very similar downcore diatom inferred pH histories (Fig.8). Although major fluctuations in the lake's pH history occurred, the ranges were similar for both pH profiles. In the 1981 and 1982 paleo-pH profiles, the diatom inferred pH ranged between 7.0 - 7.9 and pH 7.1 - 8.0 respectively. At 3 cm, the diatom inferred pH indicated a discrepancy between the 2 cores of 0.8 of a pH unit while at the 4 cm level the difference was 0.5 of a pH unit. The reasons of these differences will be discussed in the discussion section.

Figure 8. The comparison of two downcore paleo-pH profiles of Lake W1. Solid horizontal bars represent standard deviations about the mean (n=3) and broken horizontal bars represent ranges for two counts.


W1 LAKE
OBSERVED pH 6.66
1981
1982
1982
1974 Pb 210
1970
Pb210
1957 Pb 210
1936
Pb 210
AMBROSIA RISE (CIRCA 1890)
CORE DEPTH (CM)
0
2
4
6
8
10
12
14
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
DIATOM INFERRED pH

5. Downcore Diatom Stratigraphy and Diatom Inferred pH Patterns of Lakes X4, CS, U3, and W1

The diatom analyses of X4, CS, U3, and W1 lakes were conducted to measure the downcore applicability of diatom inferred pH technique and subsequently to permit the interpretation of past pH changes in these lakes. The downcore pH results of these lakes were calculated at 20 or more successive depths by using the relationship established by the regression equation shown in Fig.8A. The selection of the index alpha regression equation can be justified in terms of goodness of fit with observed pH.

A. Lake X4

To study the recent pH history of Lake X4, the subfossil diatoms were analyzed in a 20 cm long sediment core sectioned at one centimeter intervals. A total of 73 diatom taxa were identified. Only 20 of these taxa comprised more than 2% of the total diatom population. A detailed listing of the diatom taxa from Lake X4 is provided in Table 4.

a. Downcore changes in diatom population

The acidophilous diatoms were the most abundant class of pH indicator diatoms in Lake X4 (Fig.9). This group ranged between a high of 69% at 20 cm to a low of 49% at the surface of the core. The common acidophilous diatoms were *Anomoeoneis serians* var. *brachysira*, *Frustulia rhomboides*, *Pinnularia biceps*, *Stenopterobia intermedia*, and a number of *Eunotia* species. As shown in the diatom stratigraphy

Table 4. List of diatom taxa identified in the Lake X4 sediments. alp = alkaliphilous, cir = circumneutral, acp = acidophilous, acb = acidobiontic, ind = indifferent, "-" = pH indicator status unknown.

Achnanthes Bory	
minutissima Kutz.	cir
Actinella Lewis	
punctata Lewis	acb
Anomoeoneis Pfitz.	
serians var. brachysira (Breb. ex Kutz.) Hust.	acp
serians (Breb. ex Kutz.) cl.	acb
vitrea (Grun.) Ross.	alp
Caloneis Cl.	
ventricosa (Ehr.) Meist.	alp
Cyclotella Kutz.	
comta (Ehr.) Kutz.	cir
Cymbella Ag.	
angustata (W. Sm.) Cl.	alp
hauckii V. Heurck.	alp
lunata W. Sm.	cir
microcephala Grun.	cir
minuta Hilse ex Rabh.	cir
pusilla Grun.	acp
Eunotia Ehr.	
arcus Ehr.	acp
bactriana Ehr.	acb
bidentula W. Sm.	acp
bigibba Kutz.	acp
curvata (Kutz.) Lager.	acp
elegans Oster.	acp
exigua (Breb. ex Kutz.) Rabh.	acb
flexuosa Breb. ex Kutz.	acp
gibbosa Grun.	acp
hexaglyphis Ehr.	acp
incisa W. Sm. ex Greg.	acp
monodon Ehr.	acp
naegelli Migula.	acp
parallela Ehr.	acp
pectinalis var. minor (Kutz.) Rabh.	acp
pectinalis (O. Mull.) Rabh.	acp
pectinalis var. ventricosa Grun.	acp
praerupta Ehr.	acp

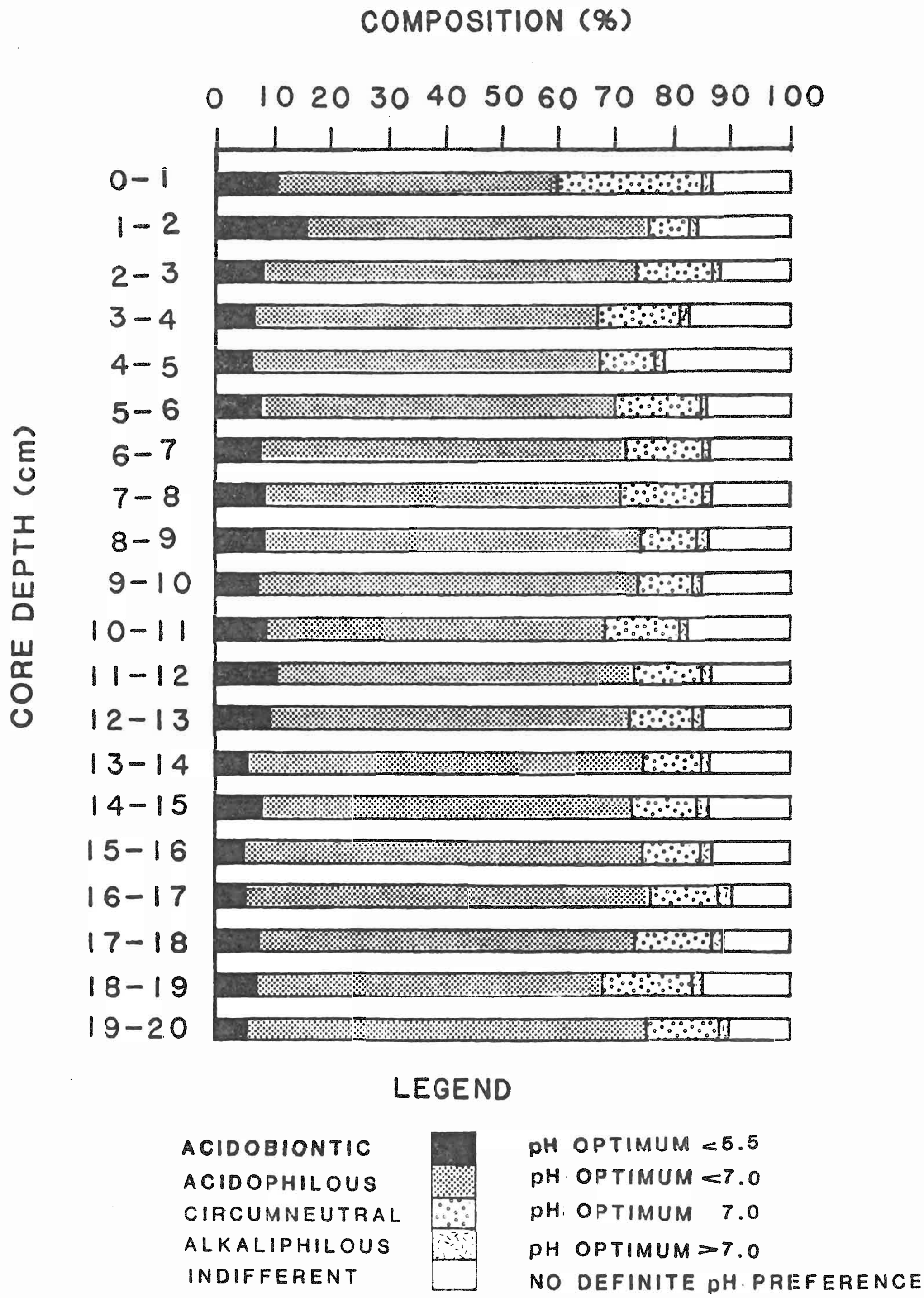
Table 4 (continued)

Eunotia Ehr.	
serra Ehr.	acp
triodon Ehr.	acp
valida Hust.	acp
vanheurckii Patr.	acp
Fragilaria Lyngb.	
constricta Ehr.	acp
Frustulia Rabh.	
rhomboides var. capitata (A. Mayer) Patr.	acp
rhomboides (Ehr.) DeT.	acp
Gomphonema Ehr.	
grunowii Patr.	-
Melosira Ag.	
distans (Ehr.) Kutz.	acp
Navicula Bory	
notha Wallace	-
radiosa var. parva Wallace	cir
radiosa Kutz.	cir
subtillissima Cl.	ind
Nedium Pfitz.	
affine (Ehr.) Pfitz.	ind
bisulcatum (Lager) Cl.	ind
iridis var. amphigomphus (Ehr.) A. Mayer	ind
iridis (Ehr.) Cl.	cir
Nitzschia Hass.	
fonticola Grun.	alp
palea (Kutz.) W. Sm.	cir
Pinnularia Ehr.	
abaujensis (Pant.) Ross	ind
abaujensis var. linearis (Hust.) Patr.	ind
abaujensis var. rostrata (Patr.) Patr.	acp
abaujensis var. subundulata (A.Mayer ex Hust.) Patr.	ind
biceps Greg.	acp
brebissonii (Kutz.) Rabh.	cir
divergens W. Sm.	acp
maior (Kutz.) Rabh.	ind
mesolepta (Ehr.) W. Sm.	acp
microstauron (Ehr.) Cl.	acp
sp.	-
Semiorbis Patr.	
hemicyclus (Ehr.) Patr.	acb

Table 4 (continued)

Stauroneis Ehr.	
anceps Ehr.	cir
livingstonii Reim.	-
phoenicenteron (Nitz.) Ehr.	cir
Stenopterobia Lewis	
intermedia Lewis	acp
Surirella Turpin	
delicatissima Lewis	ind
linearis var. constricta (Ehr.) Grun.	ind
linearis W. Sm.	ind
Synedra Ehr.	
delicatissima W. Sm.	cir
Tabellaria Ehr.	
binalis (Ehr.) Grun.	acb
fenestrata (Lyngb.) Kutz.	acp
flocculosa (Roth) Kutz.	acp

Figure 9. The downcore percent composition of pH indicator and pH indifferent diatoms of Lake X4.

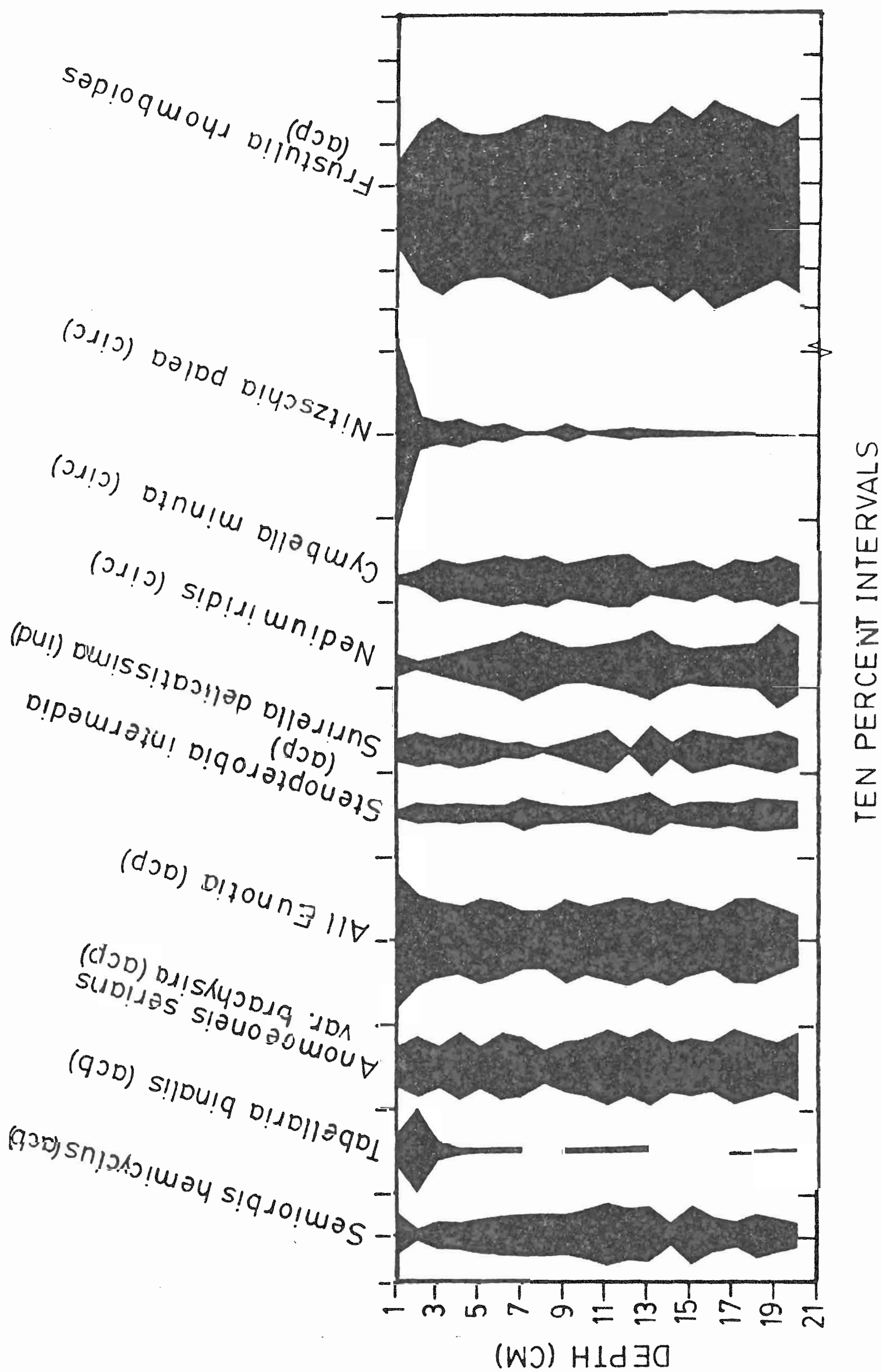

COMPOSITION (%)
0 10 20 30 40 50 60 70 80 90 100
CORE DEPTH (cm)
0-1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
8-9
9-10
10-11
11-12
12-13
13-14
14-15
15-16
16-17
17-18
18-19
19-20
LEGEND
ACIDOBIONTIC pH OPTIMUM <5.5
ACIDOPHILOUS pH OPTIMUM <7.0
CIRCUMNEUTRAL pH OPTIMUM 7.0
ALKALIPHILOUS pH OPTIMUM >7.0
INDIFFERENT NO DEFINITE pH PREFERENCE

summary diagram (Fig.10), Frustulia rhomboides was the most abundant diatom in Lake X4 (22-49% of the total diatom population). Between 3-20 cm core depths, the distribution of Frustulia rhomboides remained fairly constant (49-35%), however, in the top 2 cm of the core its population declined slightly (Fig.10). The distribution of Eunotia spp. remained fairly constant over the core length with a slight decrease at the surface. During the lake's past 200 years of history, the population of two other major acidophilous diatom taxa (Anomoeoneis serians var. brachysira and Stenopterobia intermedia) remained relatively unchanged.

The acidobiontic diatom population never exceeded more than 15% of the total diatom population in Lake X4 (Fig.9). The highest acidobiontic diatom population (15%) was observed at the 2 cm level. Only two acidobiontic taxa (Semiorbis hemicyclus and Tabellaria binalis) were common. The other four acidobiontic diatoms (Actinella punctata, Anomoeoneis serians, Eunotia bactriana, and E. exigua) made only minor and sporadic contributions to the total diatom population. Tabellaria binalis was very sparse (<2%) below the 4 cm level, but at the 2 cm level its population increased abruptly to 11%. (Fig.10). At the surface of the core, Tabellaria binalis (4%) declined slightly, but its abundance was still higher than in the lower portion of the core (4-20 cm).

In Lake X4, the alkaliphilous diatoms were sparse and their population never exceeded more than 2.5% of the total (Fig.9). The only alkaliphilous diatom taxa observed in this lake were

Figure 10. Downcore butterfly diagrams of major pH indicator diatoms from Lake X4.



Frustulia rhomboides (acp)
Nitzschia palea (circ)
Cymbella minuta (circ)
Nedium iridis (circ)
Surirella delicatissima (ind)
Stenopterobia intermedia (acp)
All Eunotia (acp)
Anomoeoneis serians var. brachysira (acp)
Tabellaria binalis (acb)
Semiorbis hemicyclus (acb)
DEPTH (CM)
1
3
5
7
9
11
13
15
17
19
21
TEN PERCENT INTERVALS

Anomoeoneis vitrea, Caloneis ventricosa, Cymbella hauckii, C. angustata, and Nitzschia fonticola.

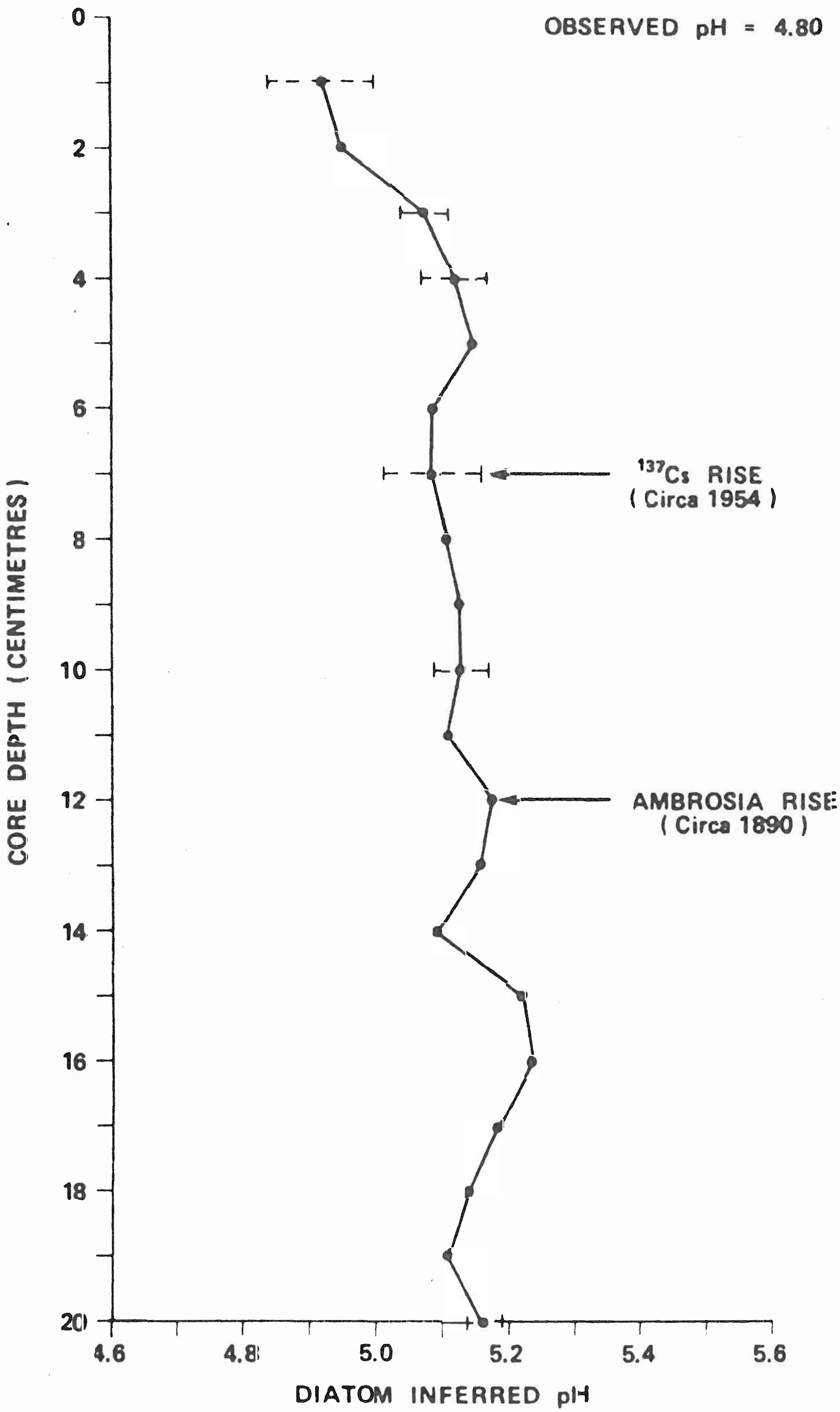
The circumneutral diatom population remained very stable (9-14%) from 20 to 2 cm core depth. However, at the surface of the core their population density suddenly increased from 14% to 25% (Fig.9). The common circumneutral diatom taxa were Cymbella minuta, Nedium iridis, and Nitzschia palea. The summarized downcore diatom stratigraphy suggested that the numbers of Cymbella minuta and Nedium iridis declined slightly in the top few centimeters of sediments (Fig.10). However, Nitzschia palea represented a sudden increase in the surface sediment.

The percent composition of pH indifferent diatoms ranged between 10 to 22% of the total diatom population at 20 and 4-5 cm respectively (Fig.9). The common pH indifferent forms were Navicula subtilissima and Surirella delicatissima. The downcore distribution of S. delicatissima indicated that its population oscillated greatly in the past (Fig.10).

b. Paleo-pH history

In Lake X4, the observed pH was 4.8 and the surface sediment diatom inferred pH was 4.9. The downcore diatom inferred pH of Lake X4 ranged from a high of 5.2 at 16 and 5 cm levels to a low of 4.9 in the most recently deposited sediment (Fig.11). Between the pre-Ambrosia and post-Ambrosia sediments, no paleo-pH changes were observed, however, there was a slight indication that in the top few centimeters of sediments the diatom inferred pH dropped from pH 5.1 to 4.9.

Figure 11. The downcore diatom inferred pH profile of Lake X4.
Horizontal bars represent ranges for two counts.



OBSERVED pH = 4.80
^{137}Cs RISE
(Circa 1954)
AMBROSIA RISE
(Circa 1890)
CORE DEPTH (CENTIMETRES)
DIATOM INFERRED pH
0
2
4
6
8
10
12
14
16
18
20
4.6
4.8
5.0
5.2
5.4
5.6

B. Lake CS

In the 16 cm long sediment core from Lake CS, the diatoms were analyzed at 0.5 cm intervals up to a depth of 5 cm. Below this the sectioning was done at 1 cm intervals. In the upper portion of the core the fine sectioning was made to obtain finer paleo-pH resolution. A species list containing the names of 88 diatom taxa identified in Lake CS is provided in Table 5. Among these diatoms, only 17 were classified as common (more than 2% of the total diatom population).

a. Downcore changes in diatom population

In Lake CS, major variations were observed in the downcore distribution of pH indicator diatom groups (Fig.12). The alkaliphilous diatoms were most abundant in this lake. Their population ranged between 28% (surface sediment) to 76% (14 cm). In the lower portion of the core (4-16 cm), the alkaliphilous diatom population was more abundant than in the sediments above it (0-4 cm). The common alkaliphilous diatom taxa were *Achnanthes linearis*, *Anomoeoneis vitrea*, *Cyclotella meneghiniana*, *Cymbella angustata*, *Fragilaria construens*, and *F. crotonensis*. The summarized downcore diatom stratigraphy (Fig.13) illustrated that *Fragilaria crotonensis* population remained fairly stable in the 16 cm long sediment core, while the abundance of *Fragilaria construens* and *Cyclotella meneghiniana* dropped significantly in the top few centimeters.

The downcore distribution of circumneutral diatoms varied greatly (Fig.12). From 5 to 16 cm core depth their abundance was relatively low

Table 5. List of diatom taxa identified in the Lake CS sediments.
alp = alkaliphilous, cir = circumneutral, acp = acidophilous, acb = acidobiontic, ind = indifferent, "-" = pH indicator status unknown.

Achnanthes Bory	
exigua Grun.	alp
flexella (Kutz.) Brun.	ind
lanceolata (Breb.) Grun.	alp
linearis (W. Sm.) Grun.	alp
Actinella Lewis	
punctata Lewis	acb
Amphora Ehr. ex Kutz.	
ovalis Kutz.	alp
Anomoeoneis Pfitz.	
follis (Ehr.) Cl.	cir
serians var. brachysira (Breb. ex Kutz.) Hust.	acp
serians (Breb. ex Kutz.) cl.	acb
vitrea (Grun.) Ross.	alp
Caloneis Cl.	
ventricosa (Ehr.) Meist.	alp
Cocconeis Ehr.	
placentula Ehr.	alp
Cyclotella Kutz.	
comta (Ehr.) Kutz.	cir
meneghiniana Kutz.	alp
Cymbella Ag.	
angustata (W. Sm.) Cl.	alp
cesatii (Rabh.) Grun. ex A.S.	cir
cistula (Ehr.) Kirchn.	alp
cuspidata Kutz.	alp
microcephala Grun.	cir
minuta Hilse ex Rabh.	cir
pusilla Grun.	acp
Diploneis Ehr.	
finnica (Ehr.) Cl.	cir
marginestriata Hust.	alp
Eunotia Ehr.	
arcus Ehr.	acp
bactriana Ehr.	acb
bidentula W. Sm.	acp
curvata (Kutz.) Lager.	acp

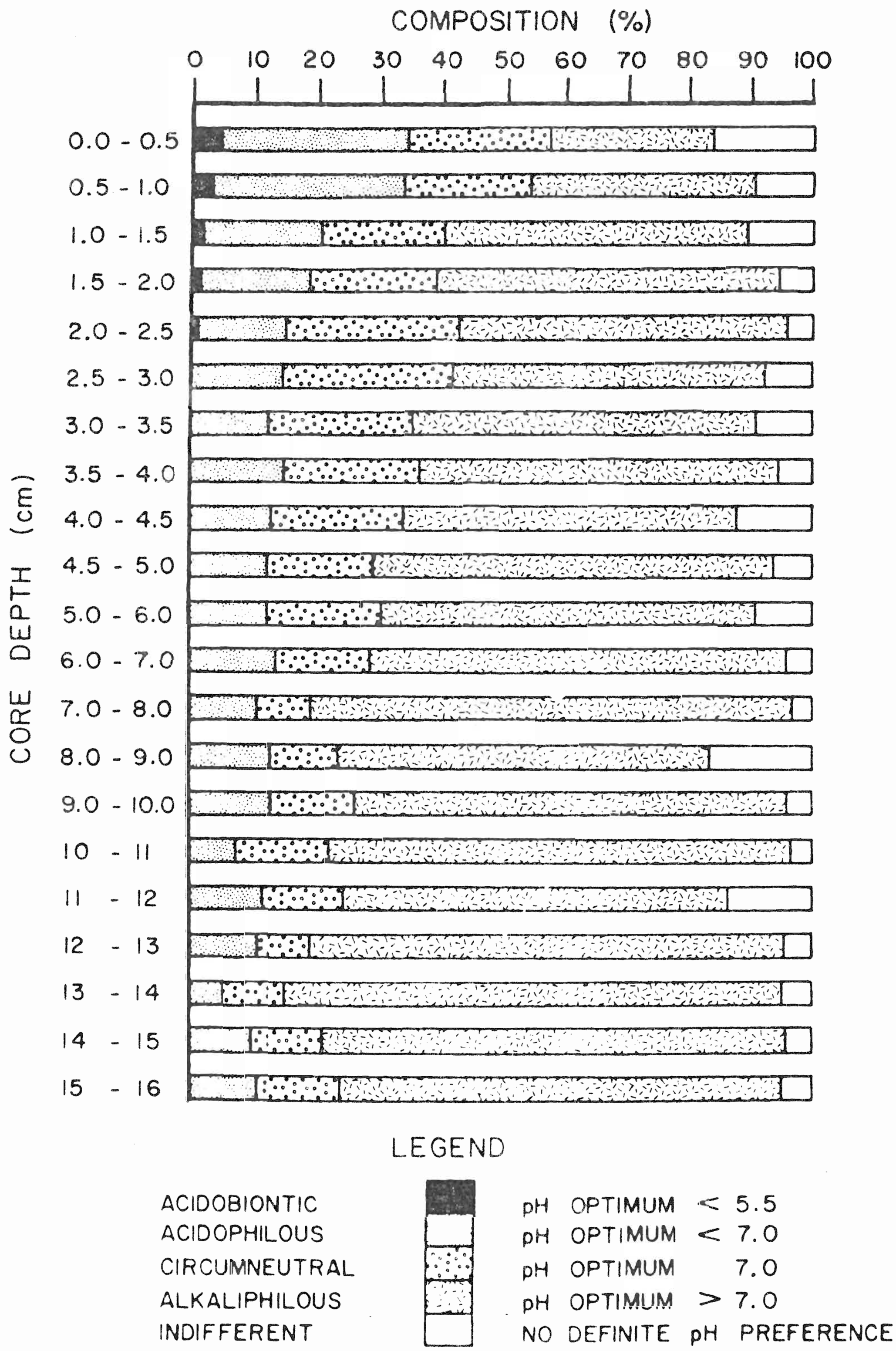
Table 5 (continued)

Eunotia Ehr.	
elegans Oster.	acp
exigua (Breb. ex Kutz.) Rabh.	acb
flexuosa Breb. ex Kutz.	acp
hexaglyphis Ehr.	acp
incisa W. Sm. ex Greg.	acp
microcephala Krasske ex Hust.	acp
naegelli Migula.	acp
pectinalis var. minor (Kutz.) Rabh.	acp
pectinalis (O. Mull.) Rabh.	acp
pectinalis var. ventricosa Grun.	acp
praerupta Ehr.	acp
serra Ehr.	acp
triodon Ehr.	acp
vanheurckii Patr.	acp
Fragilaria Lyngb.	
construens (Ehr.) Grun.	alp
crotonensis Kitton.	alp
pinnata Ehr.	alp
vaucheriae (Kutz.) Peter.	alp
virescens Ralf.	cir
Frustulia Rabh.	
rhomboides (Ehr.) DeT.	acp
Gomphonema Ehr.	
acuminatum Ehr.	alp
clevi Fricke.	ind
intricatum Kutz.	alp
subtile Ehr.	acp
truncatum Ehr.	alp
Hantzschia Grun.	
amphioxys (Ehr.) Grun.	alp
Melosira Ag.	
italica (Ehr.) Ralfs	ind
Navicula Bory	
bacillum Ehr.	alp
capitata Ehr.	alp
cuspidata (Kutz.) Kutz.	alp
notha Wallace	-
pupula Kutz.	cir
pupula var. rectangularis (Greg.) Grun.	cir
radiosa var. parva Wallace	cir
radiosa Kutz.	cir
subtillissima Cl.	ind
viridula (Kutz.) Kutz. emend. V.H.	alp
vulpina Kutz.	ind

Table 5 (continued)

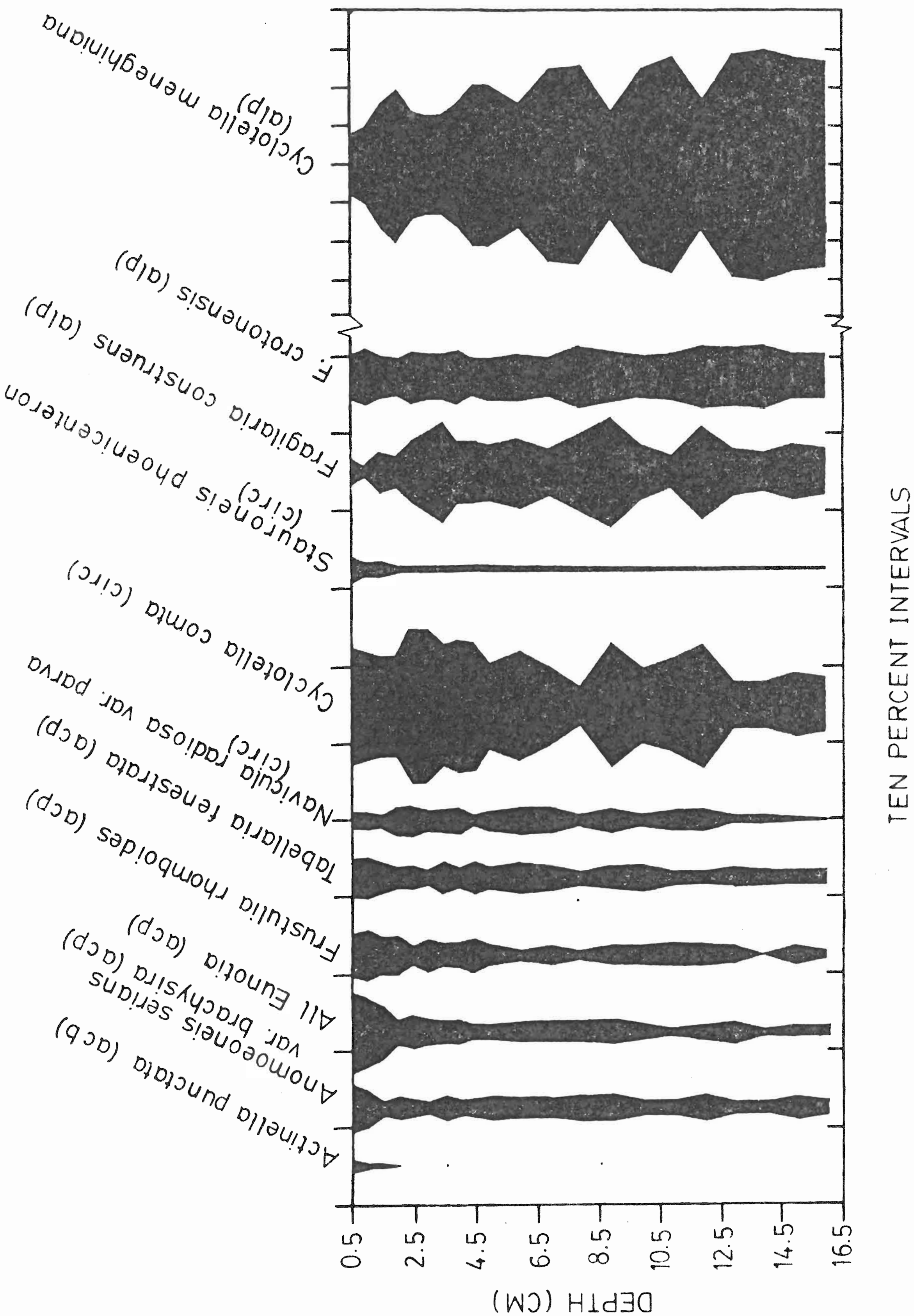
Nedium Pfitz.	
affine (Ehr.) Pfitz.	ind
hitchcockii (Ehr.) Cl.	acp
iridis var. amphigomphus (Ehr.) A. Mayer	ind
iridis (Ehr.) Cl.	cir
Nitzschia Hass.	
denticula Grun.	alp
fonticola Grun.	alp
linearis W. Sm.	alp
Peronia Breb.& Arn.	
fibula (Breb. ex Kutz) Ross	-
Pinnularia Ehr.	
abaujensis (Pant.) Ross	ind
abaujensis var. rostrata (Patr.) Patr.	acp
biceps Greg.	acp
divergens W. Sm.	acp
maior (Kutz.) Rabh.	ind
mesolepta (Ehr.) W. Sm.	acp
sp.	-
Rhopalodia O. Mull.	
parallela (Grun.) O. Mull.	alp
Semiorbis Patr.	
hemicyclus (Ehr.) Patr.	acb
Stauroneis Ehr.	
anceps Ehr.	cir
livingstonii Reim.	-
phoenicenteron (Nitz.) Ehr.	cir
Stenopterobia Lewis	
intermedia Lewis	acp
Surirella Turpin	
delicatissima Lewis	ind
linearis var. constricta (Ehr.) Grun.	ind
linearis W. Sm.	ind
Synedra Ehr.	
delicatissima W. Sm.	cir
Tabellaria Ehr.	
fenestrata (Lyngb.) Kutz.	acp
flocculosa (Roth) Kutz.	acp

Figure 12. The downcore percent composition of pH indicator and pH indifferent diatoms of Lake CS.



COMPOSITION (%)
0
10
20
30
40
50
60
70
80
90
100
CORE DEPTH (cm)
0.0 - 0.5
0.5 - 1.0
1.0 - 1.5
1.5 - 2.0
2.0 - 2.5
2.5 - 3.0
3.0 - 3.5
3.5 - 4.0
4.0 - 4.5
4.5 - 5.0
5.0 - 6.0
6.0 - 7.0
7.0 - 8.0
8.0 - 9.0
9.0 - 10.0
10 - 11
11 - 12
12 - 13
13 - 14
14 - 15
15 - 16
LEGEND
ACIDOBIONTIC pH OPTIMUM < 5.5
ACIDOPHILOUS pH OPTIMUM < 7.0
CIRCUMNEUTRAL pH OPTIMUM 7.0
ALKALIPHILOUS pH OPTIMUM > 7.0
INDIFFERENT NO DEFINITE pH PREFERENCE

Figure 13. Downcore butterfly diagrams of major pH indicator diatoms from Lake CS.


Cyclotella meneghiniana (alp)
F. crotonensis (alp)
Fragilaria construens (alp)
Stauroneis phoenicenteron (circ)
Cyclotella comta (circ)
Navicula radiosa var. parva (circ)
Tabellaria fenestrata (acp)
Frustulia rhomboides (acp)
All Eunotia (acp)
Anomoeoneis serians var. brachysira (acp)
Actinella punctata (acb)
TEN PERCENT INTERVALS
0.5
2.5
4.5
6.5
8.5
10.5
12.5
14.5
16.5
DEPTH (CM)

(8-18%), but above the 5 cm level the circumneutral diatom abundance increased significantly (20 to 28%). In Lake CS, only 4 circumneutral diatom taxa were common (*Cyclotella comta*, *Cymbella cesatii*, *Navicula radiosa* var. *parva*, and *Stauroneis phoenicenteron*). Among these circumneutral diatoms, only *Cymbella cesatii* accounted for less than 3% of the total diatom sum. From Fig.13 it is evident that in Lake CS, *Cyclotella comta* was the second most abundant diatom. The abundance of *Cyclotella comta* started to increase from 12 cm and peaked at 3.0 and 2.5 cms. The population declined slightly at 2 cm and then remained fairly constant. Although the pattern was less distinct than *Cyclotella comta*, the abundance of *Navicula radiosa* var. *parva* started to increase at the 12 cm level and gained its maximum density at 2.5 cm (Fig.13). Between 16 and 2 cm, the distribution of *Stauroneis phoenicenteron* remained very stable, but in the top 2 cms its population significantly increaesd (Fig.13).

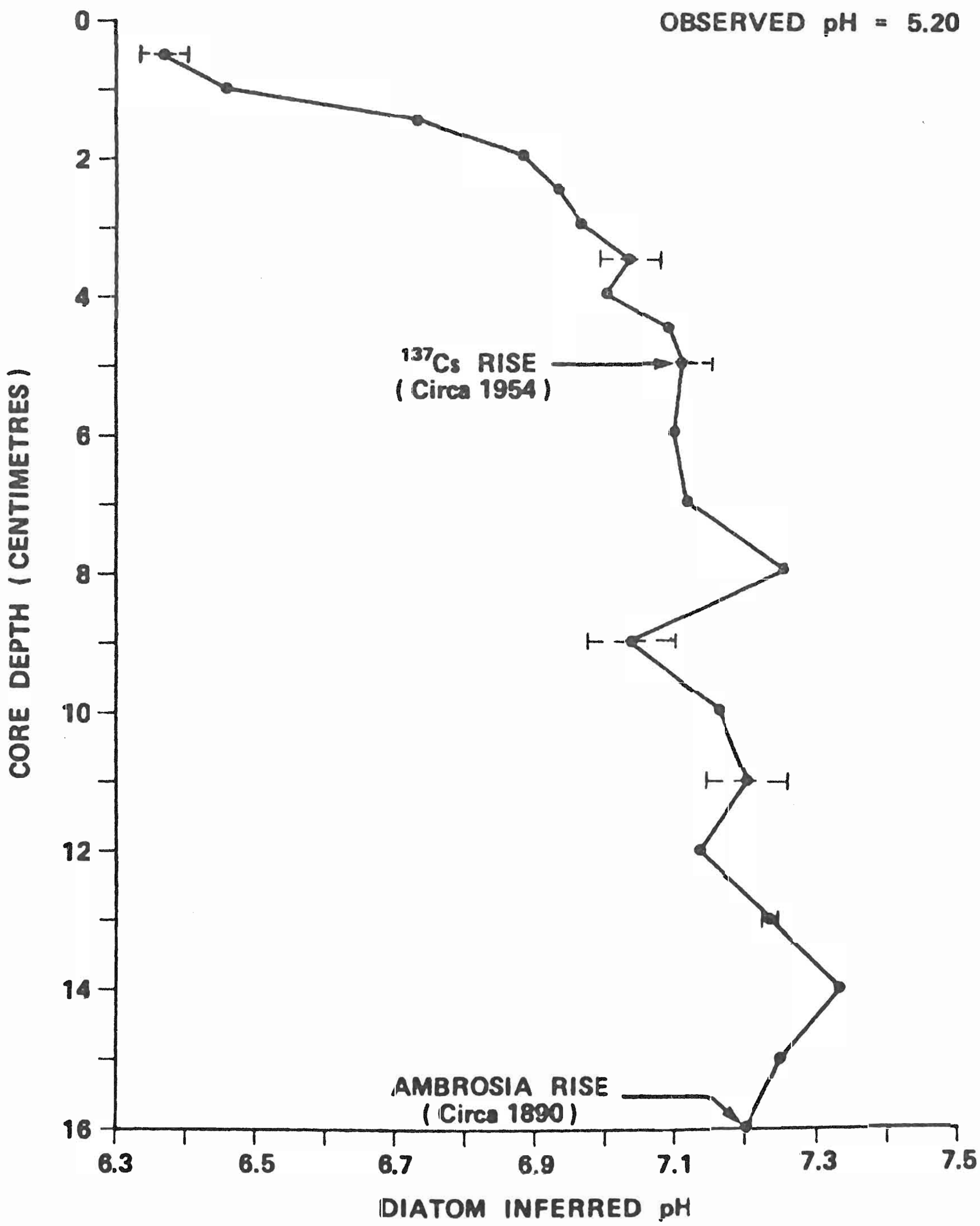
In Lake CS, the acidophilous diatom population also greatly varied in the past. Between 16 and 4 cm levels, the population ranged from a low of 5% (14 cm) to a high of 14% (4 cm, Fig.12). However, from 3.5 cm level (12%), the acidophilous diatom population successively increaesd and peaked at its highest value (30%) in the most recently deposited sediment. The common acidophilous diatoms were *Anomoeoneis serians* var. *brachysira*, *Eunotia flexuosa*, *Frustulia rhomboides*, and *Tabellaria fenestrata*. Although in Lake CS 16 acidophilous *Eunotia* species were identified, only *E. flexuosa* attained a population density of 2% or more. The abundace of all common acidophilous diatom taxa distinctly increased in the top few centimeters (Fig.13).

Although the acidobiontic diatom population never exceeded more than 5% of the total, it demonstrated the most interesting downcore distribution pattern (Fig.12). From 16 to 3 cm core depth, the acidobiontic diatoms were only present in trace amounts (<0.5%), but from 2.5 cm (1%), their population successively increased and gained its maximum abundance (5%) in the most recently deposited sediment. *Actinella punctata*, *Anomoeoneis serians*, *Eunotia exigua*, and *E. bactriana* were the only acidobiontic diatom taxa present in Lake CS. None of these acidobiontic species attained a population size of 2%. Because *Actinella punctata* was the most abundant acidobiontic diatom of Lake CS, it was included in the downcore butterfly diagrams (Fig.13).

b. Paleo-pH history

In Lake CS, the observed lake pH was 5.2 and the surface sediment diatom inferred pH was 6.2. In this lake, the diatom inferred pH remained very constant (pH 7.1-7.3) between 16 (circa 1890) and 5 cm (circa 1954) core depths (Fig.14). However, from the 5 cm level the diatom inferred pH significantly dropped ($p=<0.01$) towards the surface of the core. Over the last 30 years the diatom inferred pH of Lake CS has dropped from 7.1 to 6.4 (Fig.14).

Figure 14. The downcore diatom inferred pH profile of Lake CS. Broken horizontal bars represent ranges for two counts and solid horizontal bars represent standard deviations about the mean (n=3).


OBSERVED pH = 5.20
^{137}Cs RISE
(Circa 1954)
AMBROSIA RISE
(Circa 1890)
CORE DEPTH (CENTIMETRES)
0
2
4
6
8
10
12
14
16
6.3
6.5
6.7
6.9
7.1
7.3
7.5
DIATOM INFERRED pH

C. Lake U3

In the 20 cm long sediment core of Lake U3 the diatoms were studied at 1 cm intervals. A total of 105 diatom taxa were identified, but only 19 of these were common (>2% of the total). A species list containing the names of identified diatom taxa is given in Table 6.

a. Downcore changes in diatom population

In Lake U3 no major variations were seen in the distribution of pH indicator diatom groups (Fig.15). The alkaliphilous diatoms were most abundant in this lake and their percent composition ranged between 41% at the surface to 68% in the 17 cm deep sediments of this core. The common alkaliphilous diatom taxa were *Achnanthes lanceolata*, *Anomoeoneis vitrea*, *Cyclotella bodanica*, *C. meneghiniana*, *Fragilaria construens*, *F. construens* var. *venter*, *F. pinnata*, and *Melosira granulata*. *Fragilaria construens* and *Melosira granulata* were the two most abundant diatoms in Lake U3 (Fig.16). These two species shared 10-23% and 11-25% of the total diatom population respectively. Figure 16 illustrates that there were no distinct patterns in the downcore abundance of *Cyclotella bodanica*, *C. meneghiniana*, *Fragilaria construens*, *F. pinnata*, and *Melosira granulata* (Fig.16).

The circumneutral diatoms were identified as the second most abundant group in Lake U3 (Fig.15). Their population ranged between 16 and 42% of the total. From 5 to 20 cm of core depth gave no definite pattern in the distribution of circumneutral diatoms, but

Table 6. List of diatom taxa identified in the Lake U3 sediments. alp = alkaliphilous, cir = circumneutral, acp = acidophilous, acb = acidobiontic, ind = indifferent, "-" = pH indicator status unknown.

Achnanthes Bory	
exigua Grun.	alp
flexella (Kutz.) Brun.	ind
lanceolata (Breb.) Grun.	alp
linearis (W. Sm.) Grun.	alp
minutissima Kutz.	cir
Amphora Ehr. ex Kutz.	
ovalis Kutz.	alp
Anomoeoneis Pfitz.	
follis (Ehr.) Cl.	cir
serians var. brachysira (Breb. ex Kutz.) Hust.	acp
serians (Breb. ex Kutz.) cl.	acb
vitrea (Grun.) Ross.	alp
zellensis (Grun.) Cl.	-
Asterionella Hass.	
formosa Hass	ind
Caloneis Cl.	
ventricosa (Ehr.) Meist.	alp
Cocconeis Ehr.	
placentula Ehr.	alp
pediculus Ehr.	alp
Cyclotella Kutz.	
bodanica Eulenst.	alp
comta (Ehr.) Kutz.	cir
meneghiniana Kutz.	alp
stelligera (Cl.& Grun.) V.H.	alp
Cymbella Ag.	
angustata (W. Sm.) Cl.	alp
cesatii (Rabh.) Grun. ex A.S.	cir
cistula (Ehr.) Kirchn.	alp
cuspidata Kutz.	alp
cymbioformis Ag.	ind
hauckii V. Heurck.	alp
lunata W. Sm.	cir
microcephala Grun.	cir
minuta Hilse ex Rabh.	cir
pusilla Grun.	acp

Table 6 (continued)

Diatoma Bory nom. cons. Loureiro	
hiemale (Roth) Heib.	alp
Diploneis Ehr.	
finnica (Ehr.) Cl.	cir
smithi (Breb. ex. W. Sm.) Cl.	cir
Epithemia Breb.	
argus var. alpestris Grun.	alp
sorex Kutz.	alp
Eunotia Ehr.	
elegans Oster.	acp
flexuosa Breb. ex Kutz.	acp
incisa W. Sm. ex Greg.	acp
pectinalis var. minor (Kutz.) Rabh.	acp
pectinalis (O. Mull.) Rabh.	acp
pectinalis var. ventricosa Grun.	acp
praerupta Ehr.	acp
triodon Ehr.	acp
Fragilaria Lyngb.	
brevistriata Grun.	alp
constricta Ehr.	acp
construens var. binodis (Ehr.) Grun.	ind
construens (Ehr.) Grun.	alp
construens var. venter (Ehr.) Grun.	alp
crotonensis Kitton.	alp
pinnata Ehr.	alp
vaucheriae (Kutz.) Peter.	alp
Frustulia Rabh.	
rhomboides (Ehr.) DeT.	acp
Gomphonema Ehr.	
acuminatum Ehr.	alp
clevi Fricke.	ind
grunowii Patr.	-
intricatum Kutz.	alp
subtile Ehr.	acp
truncatum Ehr.	alp
Melosira Ag.	
distans (Ehr.) Kutz.	acp
granulata (Ehr.) Ralfs	alp
italica (Ehr.) Ralfs	ind
Navicula Bory	
aurora Sov.	alp
bacillum Ehr.	alp
capitata Ehr.	alp

Table 6 (continued)

Navicula Bory	
cuspidata (Kutz.) Kutz.	alp
elginensis var. rostrata (A. Mayer) Patr.	-
gottlandica Grun.	cir
laterostrata Hust.	-
notha Wallace	-
pupula var. capitata Skv.& Mayer	cir
pupula var. rectangularis (Greg.) Grun.	cir
radiosa var. parva Wallace	cir
radiosa Kutz.	cir
subtillissima Cl.	ind
viridula (Kutz.) Kutz. emend. V.H.	alp
vulpina Kutz.	ind
Nedium Pfitz.	
affine (Ehr.) Pfitz.	ind
bisulcatum (Lager) Cl.	ind
hitchcockii (Ehr.) Cl.	acp
iridis var. amphigomphus (Ehr.) A. Mayer	ind
iridis (Ehr.) Cl.	cir
Nitzschia Hass.	
denticula Grun.	alp
fonticola Grun.	alp
linearis W. Sm.	alp
sinuata (W. Sm.) Grun.	cir
Pinnularia Ehr.	
abaujensis (Pant.) Ross	ind
abaujensis var. rostrata (Patr.) Patr.	acp
biceps Greg.	acp
formica (Ehr.) Patr.	-
maior (Kutz.) Rabh.	ind
mesolepta (Ehr.) W. Sm.	acp
Rhopalodia O. Mull.	
parallela (Grun.) O. Mull.	alp
Semiorbis Patr.	
hemicyclus (Ehr.) Patr.	acb
Stauroneis Ehr.	
acuta W. Sm.	alp
anceps Ehr.	cir
livingstonii Reim.	-
phoenicenteron (Nitz.) Ehr.	cir
Stenopterobia Lewis	
intermedia Lewis	acp

Table 6 (continued)

Surirella Turpin	
linearis var. constricta (Ehr.) Grun.	ind
linearis W. Sm.	ind
Synedra Ehr.	
delicatissima W. Sm.	cir
parasitica (W. Sm.) Hust.	alp
ulna (Nitz.) Ehr.	alp
Tabellaria Ehr.	
fenestrata (Lyngb.) Kutz.	acp
flocculosa (Roth) Kutz.	acp

Figure 15. The downcore percent composition of pH indicator and pH indifferent diatoms of Lake U3.

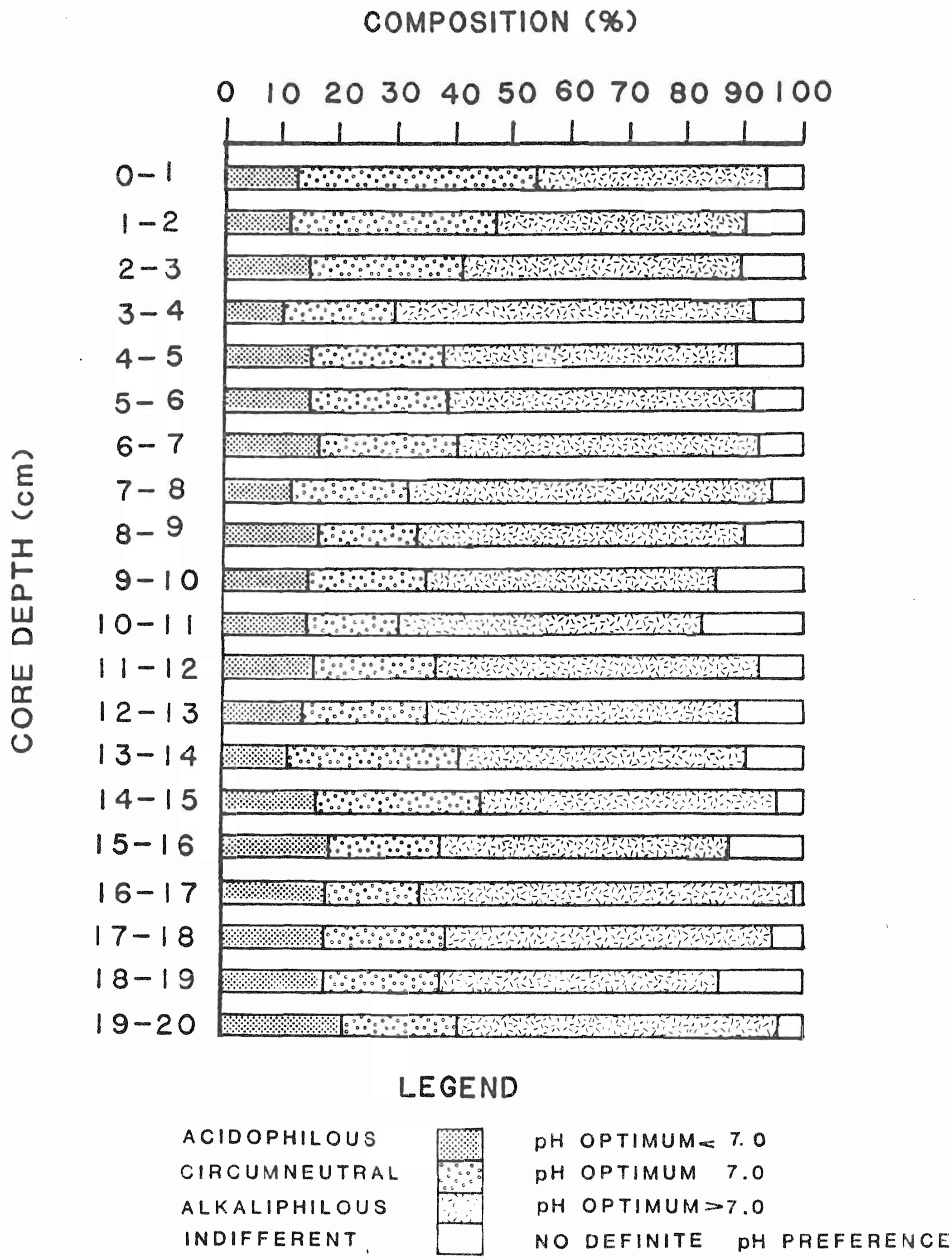
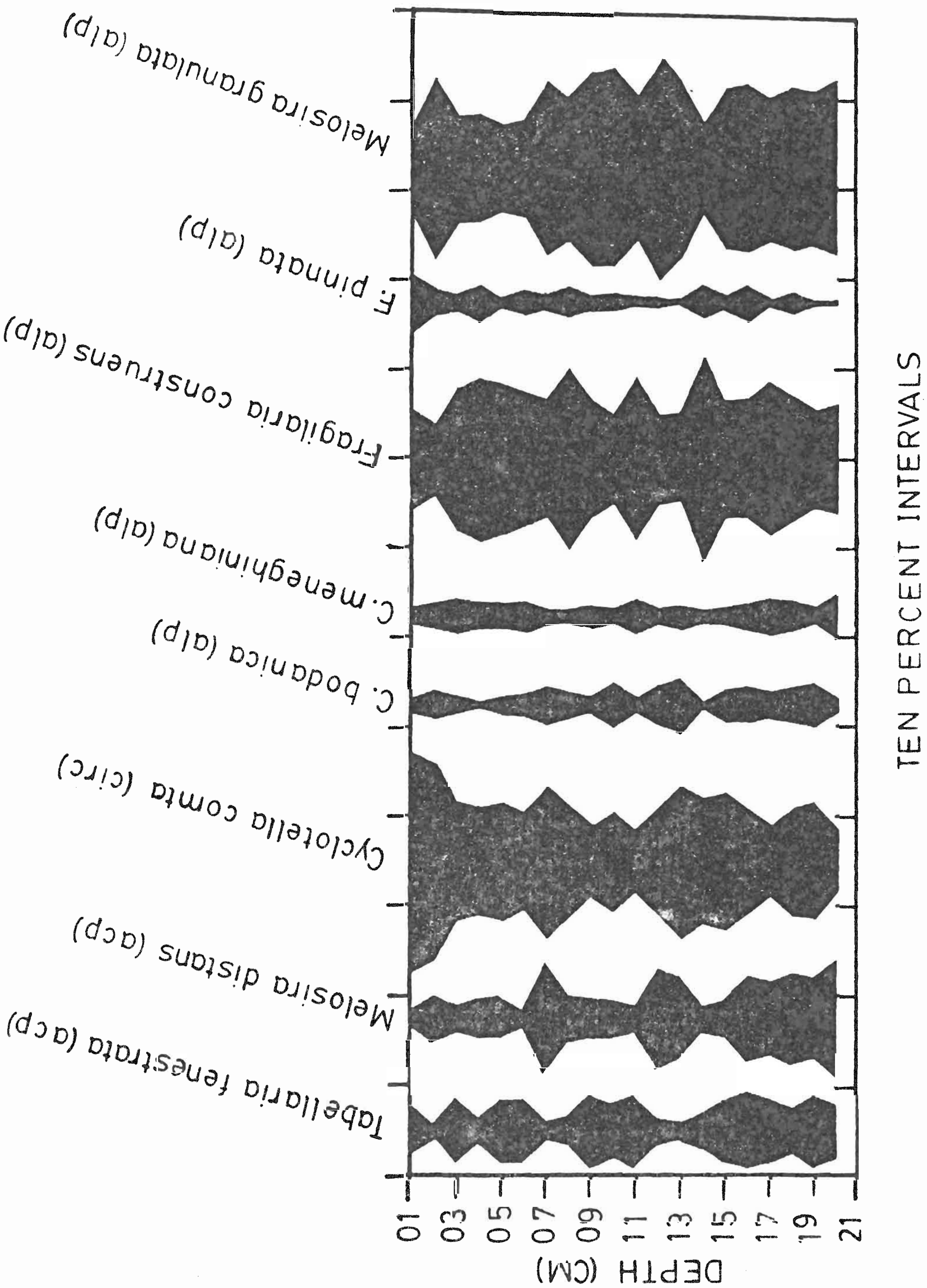

COMPOSITION (%)
0 10 20 30 40 50 60 70 80 90 100
CORE DEPTH (cm)
0-1
1-2
2-3
3-4
4-5
5-6
6-7
7-8
8-9
9-10
10-11
11-12
12-13
13-14
14-15
15-16
16-17
17-18
18-19
19-20
LEGEND
ACIDOPHILOUS pH OPTIMUM < 7.0
CIRCUMNEUTRAL pH OPTIMUM 7.0
ALKALIPHILOUS pH OPTIMUM > 7.0
INDIFFERENT NO DEFINITE pH PREFERENCE

Figure 16. Downcore butterfly diagrams of major pH indicator diatoms from Lake U3.



Melosira granulata (alp)
F. pinnata (alp)
Fragilaria construens (alp)
C. meneghiniana (alp)
C. bodanica (alp)
Cyclotella comta (circ)
Melosira distans (acp)
Tabellaria fenestrata (acp)
TEN PERCENT INTERVALS
01 03 05 07 09 11 13 15 17 19 21
DEPTH (CM)

above the 4 cm level (18%) the circumneutral diatom population gradually increased and reached its maximum value (42%) at the surface of the core. The common circumneutral diatoms were *Achnanthes minutissima*, *Cyclotella comta*, *Cymbella minuta*, and *Navicula pupula* var. *rectangularis*. Among these common circumneutral diatoms, only *Cyclotella comta* attained a population density of 3% of the total. In general, *Cyclotella comta* was the third most abundant diatom in Lake U3 (11-21%). However, this taxon was most abundant in the top 2 cms of the core (Fig.15).

In Lake U3, the acidophilous diatoms were less abundant than the alkaliphilous and circumneutral forms (Fig.15). The acidophilous diatoms only contributed 11-21% of the total diatom population. The common acidophilous taxa were *Anomoeoneis serians* var. *brachysira*, *Melosira distans*, and *Tabellaria fenestrata*. The composition of *Anomoeoneis serians* var. *brachysira* was always less than 3% of the total. *Melosira distans* and *Tabellaria fenestrata* were fourth (3-13%) and fifth (2-9%) in relative abundance (Fig.16). These two most abundant acidophilous diatoms did not show any definite downcore distribution pattern.

Except for the single individuals of *Anomoeoneis serians* and *Semiorbis hemicyclus* at 3 and 5 cm levels, the acidobiontic diatoms were absent from Lake U3.

b. Paleo-pH history

In Lake U3, the observed lake pH was 7.05 and the surface sediment diatom inferred pH was 7.0. The downcore pH profile represented a very stable paleo-pH history for Lake U3 (Fig.17). Over the last 100-140 years the diatom inferred pH in Lake U3 has fluctuated only 0.3 of a pH unit. Moreover, no significant pH changes were observed between the pre-*Ambrosia* and post-*Ambrosia* sediments. The highest recorded diatom inferred pH (7.2) was at the 4 cm level and the lowest (pH 6.9) was at the 19 cm level.

D. Lake W1

In the 15 cm long sediment core from Lake W1, the diatoms were analyzed at 20 different depths. The first 10 samples were studied at 0.5 cm intervals and thereafter the analysis was done at 1 cm intervals. A total of 66 diatom taxa were encountered in this lake and among them only 21 were common (>2% of the total). A complete listing of the diatom taxa found in Lake W1 is provided in Table 7.

a. Downcore changes in diatom population

In Lake W1, the percent composition of different pH indicator diatom groups has varied widely over the past 30 years (Fig.18). The alkaliphilous diatoms were most abundant. They represented a population density of 23-66% of the total. The downcore distribution of the alkaliphilous diatoms remained very stable (23-30%) between 15 and 8 cm core depths, but at 7 cm their population greatly increased to 66%.

Figure 17. The downcore diatom inferred pH profile of Lake U3. Horizontal bars represent ranges for two counts.

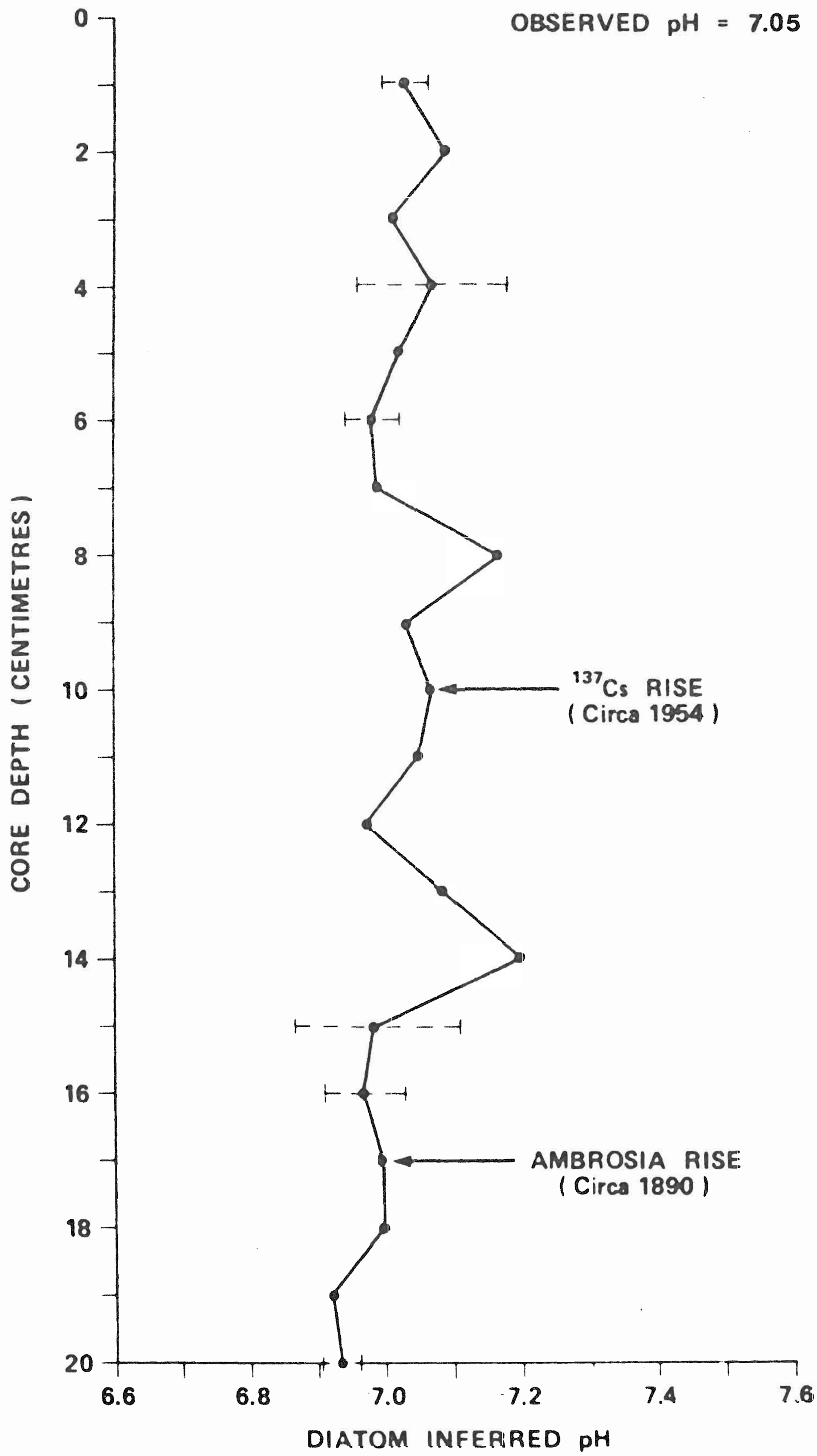

OBSERVED pH = 7.05
137Cs RISE
(Circa 1954)
AMBROSIA RISE
(Circa 1890)
CORE DEPTH (CENTIMETRES)
0
2
4
6
8
10
12
14
16
18
20
6.6
6.8
7.0
7.2
7.4
7.6
DIATOM INFERRED pH

Table 7. List of diatom taxa identified in the Lake W1 sediments. alp = alkaliphilous, cir = circumneutral, acp = acidophilous, acb = acidobiontic, ind = indifferent, "-" = pH indicator status unknown.

Achnanthes Bory	
exigua Grun.	alp
flexella (Kutz.) Brun.	ind
linearis (W. Sm.) Grun.	alp
minutissima Kutz.	cir
Amphora Ehr. ex Kutz.	
ovalis Kutz.	alp
Anomoeoneis Pfitz.	
serians var. brachysira (Breb. ex Kutz.) Hust.	acp
vitrea (Grun.) Ross.	alp
zellensis (Grun.) Cl.	-
Asterionella Hass.	
formosa Hass	ind
Caloneis Cl.	
ventricosa (Ehr.) Meist.	alp
Cyclotella Kutz..	
comta (Ehr.) Kutz.	cir
meneghiniana Kutz.	alp
Cymbella Ag.	
angustata (W. Sm.) Cl.	alp
cisatii (Rabh.) Grun. ex A.S.	cir
cistula (Ehr.) Kirchn.	alp
cuspidata Kutz.	alp
helvetica Kutz.	alp
microcephala Grun.	cir
minuta Hilse ex Rabh.	cir
Diploneis Ehr.	
finnica (Ehr.) Cl.	cir
Epithemia Breb.	
argus var. alpestris Grun.	alp
Eunotia Ehr.	
bigibba Kutz.	acp
incisa W. Sm. ex Greg.	acp
pectinalis (O. Mull.) Rabh.	acp
pectinalis var. ventricosa Grun.	acp
praerupta Ehr.	acp

Table 7 (continued)

Fragilaria Lyngb.	
construens (Ehr.) Grun.	alp
pinnata Ehr.	alp
vaucheriae (Kutz.) Peter.	alp
virescens Ralf.	cir
Frustulia Rabh.	
rhomboides (Ehr.) DeT.	acp
Gomphonema Ehr.	
intricatum Kutz.	alp
subtile Ehr.	acp
truncatum Ehr.	alp
Melosira Ag.	
granulata (Ehr.) Ralfs	alp
Navicula Bory	
aurora Sov.	alp
bicephala Hust.	-
cuspidata (Kutz.) Kutz.	alp
elginensis var. rostrata (A. Mayer) Patr.	-
peregrina (Ehr.) Kutz.	cir
pupula var. rectangularis (Greg.) Grun.	cir
radiosa var. parva Wallace	cir
radiosa Kutz.	cir
subtillissima Cl.	ind
Nedium Pfitz.	
affine (Ehr.) Pfitz.	ind
bisulcatum (Lager) Cl.	ind
hitchcockii (Ehr.) Cl.	acp
iridis var. amphigomphus (Ehr.) A. Mayer	ind
iridis (Ehr.) Cl.	cir
Nitzschia Hass.	
denticula Grun.	alp
fonticola Grun.	alp
linearis W. Sm.	alp
Pinnularia Ehr.	
abaujensis (Pant.) Ross	ind
abaujensis var. rostrata (Patr.) Patr.	acp
biceps Greg.	acp
divergens W. Sm.	acp
formica (Ehr.) Patr.	-
maior (Kutz.) Rabh.	ind
microstauron (Ehr.) Cl.	acp

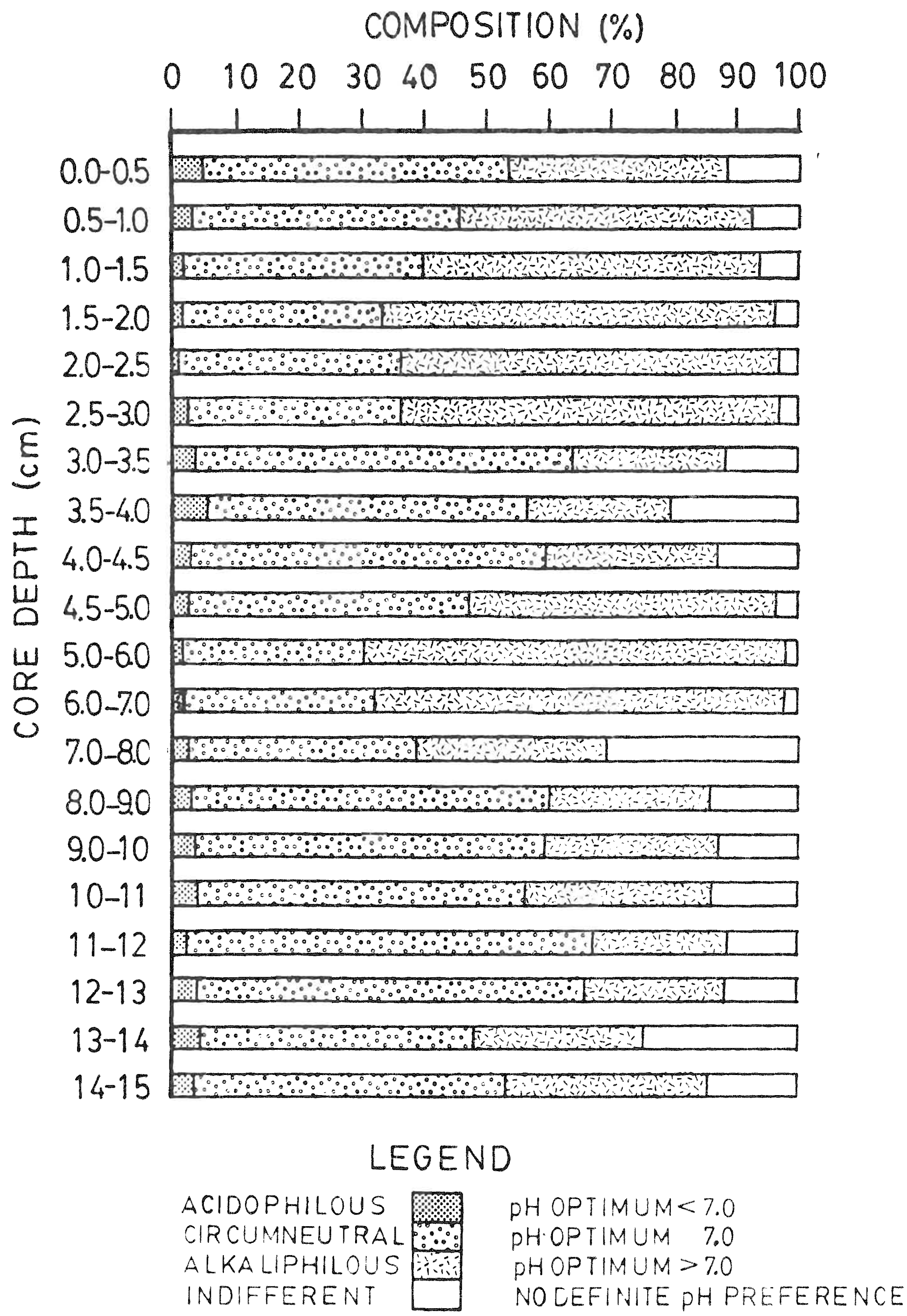
Table 2 (continued)

Rhopalodia O. Mull.	
parallela (Grun.) O. Mull.	alp

Table 7 (continued)

Stauroneis Ehr.	
phoenicenteron (Nitz.) Ehr.	cir
Surirella Turpin	
linearis var. constricta (Ehr.) Grun.	ind
linearis W. Sm.	ind
Synedra Ehr.	
delicatissima W. Sm.	cir
Tabellaria Ehr.	
fenestrata (Lyngb.) Kutz.	acp
flocculosa (Roth) Kutz.	acp

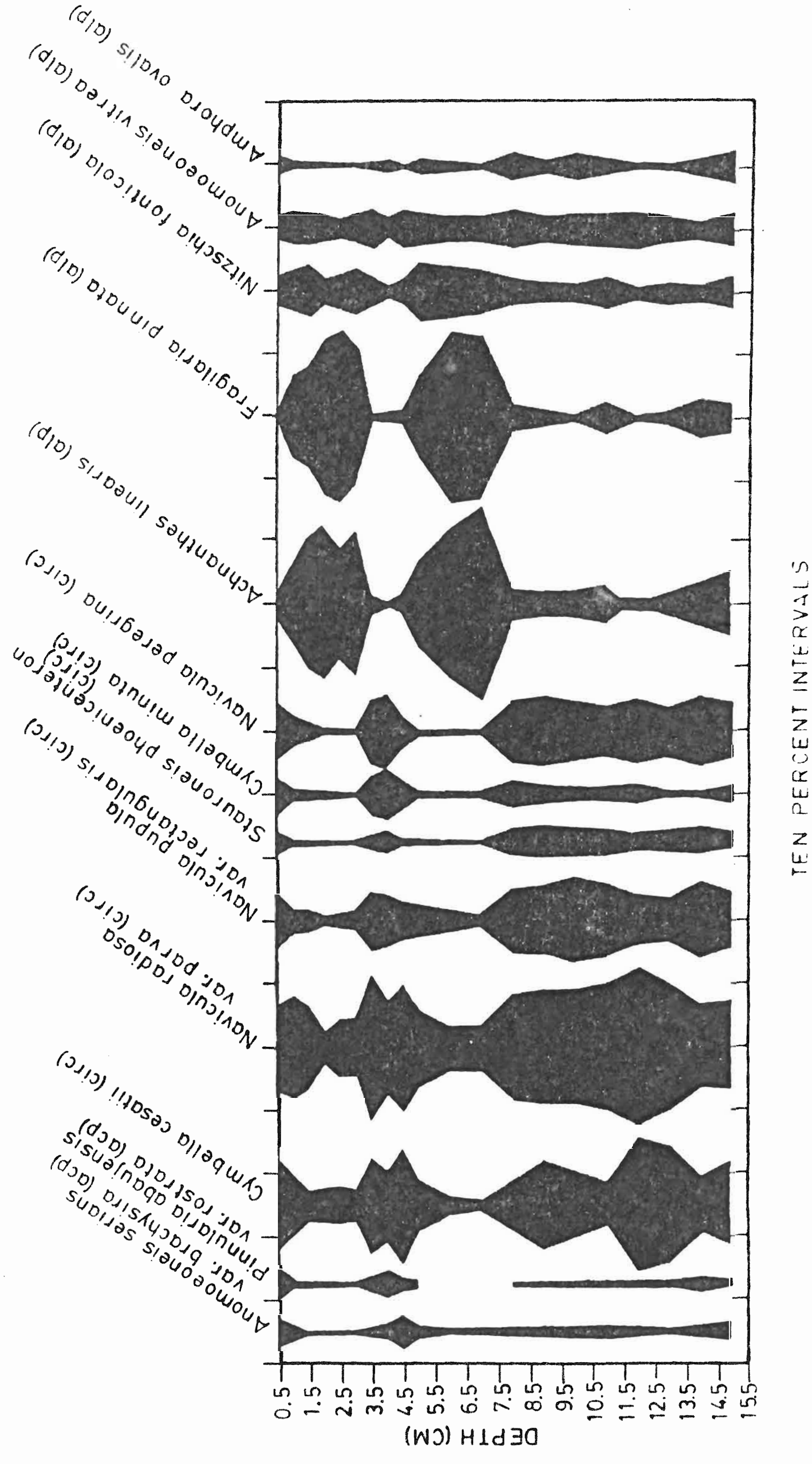
Figure 18. The downcore percent composition of pH indicator and pH indifferent diatoms of Lake W1.


COMPOSITION (%)
0 10 20 30 40 50 60 70 80 90 100
CORE DEPTH (cm)
0.0-0.5
0.5-1.0
1.0-1.5
1.5-2.0
2.0-2.5
2.5-3.0
3.0-3.5
3.5-4.0
4.0-4.5
4.5-5.0
5.0-6.0
6.0-7.0
7.0-8.0
8.0-9.0
9.0-10
10-11
11-12
12-13
13-14
14-15
LEGEND
ACIDOPHILOUS pH OPTIMUM < 7.0
CIRCUMNEUTRAL pH OPTIMUM 7.0
ALKALIPHILOUS pH OPTIMUM > 7.0
INDIFFERENT NO DEFINITE pH PREFERENCE

From the 7 cm level, the alkaliphilous diatom population gradually declined to a value of 23% at 4 and 3.5 cm samples and later the population again increased and remained stable (60-64%) at 3 and 2 cm levels. However, the population gradually declined towards the surface of the core. In Lake W1, the common alkaliphilous diatoms were Achnanthes linearis, Amphora ovalis, Anomoeoneis vitrea, Cyclotella meneghiniana, Cymbella cuspidata, C. helvetica, Fragilaria pinnata, Nitzschia fonticola, and Rhopalodia parallela. As indicated in Figure 19, Achnanthes linearis and Fragilaria pinnata were the two most abundant alkaliphilous diatoms. In decreasing order of dominance were Nitzschia fonticola, Anomoeoneis vitrea, and Amphora ovalis. Acnanthes linearis, Fragilaria pinnata, and Nitzschia fonticola demonstrated the identical downcore distribution patterns with peaks at 2-3, 6-7, and 11 cm levels (Fig.19). The downcore population of Anomoeoneis vitrea and Amphora ovalis did not follow the same pattern as that of the 3 other major alkaliphilous diatoms. The decrease of alkaliphilous diatom population at surface, 3.5-4.5, and 8-14 cm was closely mirrored by the circumneutral diatoms (Fig.19).

The circumneutral diatoms also contributed a major portion of the total diatom population. Their population size ranged from a low of 26% at 6 cm to a high of 65% at 12 cm (Fig.18). At most levels, there was an inverse relationship between the circumneutral and alkaliphilous diatom populations and thus the increasing and decreasing patterns of circumneutral diatoms were paralleled by the opposite patterns of alkaliphilous diatoms. The common circumneutral diatoms were Achnanthes minutissima, Cymbella cesatii, C. minuta, Navicula

Figure 19. Downcore butterfly diagrams of major pH indicator diatoms from Lake W1.



Amphora ovalis (alp)
Anomoeoneis vitrea (alp)
Nitzschia fonticola (alp)
Fragilaria pinnata (alp)
Achnanthes linearis (alp)
Navicula peregrina (circ)
Cymbella minuta (circ)
Stauroneis phoenicenteron (circ)
Navicula pupula var. rectangularis (circ)
Navicula radiosa var. parva (circ)
Cymbella cesatii (circ)
Pinnularia abaujensis var. rostrata (acp)
Anomoeoneis serians var. brachysira (acp)
0.5
1.5
2.5
3.5
4.5
5.5
6.5
7.5
8.5
9.5
10.5
11.5
12.5
13.5
14.5
15.5
DEPTH (CM)
TEN PERCENT INTERVALS

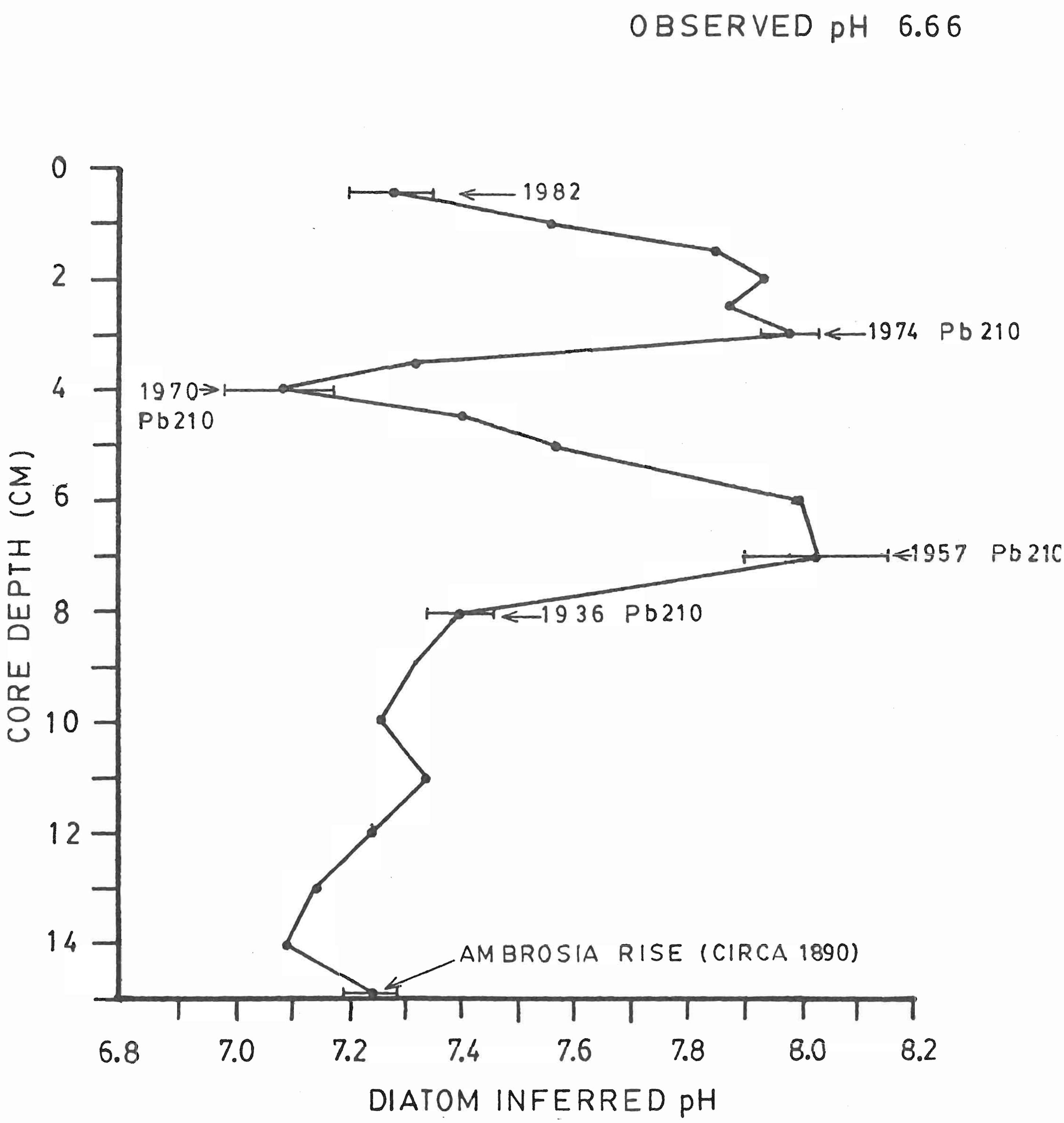
peregrina, N. pupula var. rectangularis, N. radiosa var. parva, and Stauroneis phoenicenteron. Navicula radiosa var. parva and Cymbella cesatii were the two most abundant circumneutral diatoms of Lake Wl (Fig.19). The dominance was later followed by Navicula pupula var. rectangularis, N. peregrina, Cymbella minuta, and Stauroneis phoenicenteron. In general, all the major circumneutral diatom taxa represented a similar downcore distribution pattern (Fig.19).

In Lake Wl, the acidophilous diatoms were least abundant (Fig.18). Their population size ranged from a low of 1% at 7 cm to a high of 6% at 4 cm. Interestingly, the maximum acidophilous diatom population at 4 cm level was closely associated with the lowest level of alkaliphilous diatoms observed in the 15 cm long sediment core. Both the alkaliphilous and acidophilous diatom populations remained fairly constant (3-5%) between 8 to 15 cm. However, from the 7 cm level, the acidophilous diatom population gradually increased to its maximum at 4 cm (6%) and thereafter declined to 1.5% at 2.5 cm. Between 2.5 cm and the surface, the acidophilous diatom population again increased in a regular pattern (1.5-5.0%, Fig.18). Only two acidophilous diatoms, Anomoeoneis serians var. brachysira and Pinnularia abaujensis var. rostrata attained a population density of three percent. Although Pinnularia abaujensis var. rostrata was absent at 6 and 7 cms it and A. serians var. brachysira exhibited very similar downcore distribution patterns (Fig.19). These two acidophilous diatoms showed maximum populations at 4-4.5 cms levels and at the surface of the core (Fig.19).

b. Paleo-pH history

In Lake W1, the observed lake pH was 6.66 and the surface sediment diatom inferred pH was 7.3. Downcore paleo-pH in Lake W1 fluctuated from 7.1 to 8.0 over the last 150 years. For the early period of analysis (15-8 cm), the diatom inferred pH remained relatively stable (7.1-7.4). However, from 8 to 7 cm (circa 1936 - 1957), the diatom inferred pH significantly increased ($p=<0.01$) from a pH value of 7.4 to 8.0. The second significant ($p=<0.01$) paleo-pH shift occurred between circa 1957 (7 cm) and circa 1970 (4 cm). Within this period, the diatom inferred pH dropped from 8.0 to 7.1. Between 4 and 3 cm levels (circa 1970-1974), the diatom inferred pH again significantly increaesd ($p=<0.01$) from 7.1 to 8.0. From the 3 cm level, the diatom inferred pH significantly dropped ($p=<0.01$), and in the most recently deposited sediment (0.5 cm) the diatom inferred pH was 7.3 (Fig.20).

Figure 20. The downcore diatom inferred pH profile of Lake W1. Horizontal bars represent standard deviations about the mean (n=3).


OBSERVED pH 6.66
1982
1974 Pb 210
1970
Pb210
1957 Pb 210
1936 Pb210
AMBROSIA RISE (CIRCA 1890)
CORE DEPTH (CM)
0
2
4
6
8
10
12
14
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
DIATOM INFERRED pH

DISCUSSION

1. Surface Sediment Diatoms

The surface sediment diatom analysis of 28 study lakes indicates that even though each lake has widely different aquatic environment and characteristic diatom assemblages, a definite relationship exists between the lake's pH and its percent composition of different pH indicator diatom groups (Fig.4). Thus lake pH is one of the most important factors affecting the variation in diatom species composition. Similar observations were reported by Berge (1980) and Davis et al. (1980). In my study the observed relationship between lake pH, and diatom species composition and relative abundance fulfills the prerequisite raised by Norton et al. (1981) and Vaughan et al. (1982), who noted the need to demonstrate the relationship between the pH preference of diatoms and observed lake pH.

A. Acid indicator diatoms

In the present study acidobiontic diatoms attained their optimum population at a slightly lower pH (pH <4.9) than the one reported by Hustedt (pH <5.5). Four common acidobiontic diatoms (*Semiorbis hemicyclus*, *Anomoeoneis serians*, *Actinella punctata*, *Tabilaria binalis*) were observed in the Algoma study lakes (Fig.6).

A controversy exists about the pH status of *Anomoeoneis serians*. Alhonen (1972) and Foged (1979) classified *A. serians* as an acidophilic diatom. Patrick and Reimer (1966) suggested that this diatom can be grouped as either acidophilic or acidobiontic while

Merilainen (1967) classified it as acidobiontic. My results (Fig.6) supported Merilainen's (1967) findings.

Although most of the common acidophilous diatom taxa developed their maximum population at a pH below 6.4, Anomoeoneis serians var. brachysira and Tabellaria fenestrata peaked at a pH around 7.0 (Fig.6). Anomoeoneis serians var. brachysira, an acidophilic diatom was about 8-10% of the population in lakes with a pH range of 5.4 to 6.2, despite one instance of an elevated population in a circumneutral lake. Similar observations were also indicated by Norton et al. (1981).

Tabellaria fenestrata gained its maximum abundance in circumneutral waters, however, at low pH the population was still high (Fig.6). This is in agreement with Cholnoky's (1968) explanation that T. fenestrata displays a wide pH preference and can have a population optimum at any pH between 5.0 and 7.1. Tabellaria fenestrata also increases at higher nutrient levels (Patrick and Reimer 1966). Patrick and Reimer (1966) and Kling and Holmgren (1972) explained that T. fenestrata prefers mesotrophic to eutrophic waters and Stoermer and Yang (1970) mentioned that this species is an indicator of eutrophic waters. However, Rawson (1956) described this taxon in the oligotrophic lakes of western Canada. Thus it can be suggested that at a lower pH T. fenestrata acts as an acidophilic pH indicator, but in circumneutral lakes this taxon can become nutrient sensitive and hence looses its pH indicator quality. Alternatively, there may be two ecotypes of this species. Autecological studies are clearly warrented.

In general, whenever the acidobiontic diatom population increased, there was a relative decrease in the size of the acidophilous diatom population (Fig.4). However, in the acidic lakes (pH <5.6) this kind of relationship was not observed. The most probable reason for the absence of any definite pattern can be the extent of the recent pH shift in these lakes. If in an acidic lake the pH was constant in the past, the stable environment would provide an equilibrium between acidophilic and acidobiontic diatom populations as expected theoretically. However, if lake pH has rapidly dropped, the equilibrium will not establish itself due to the lag period required for the shift in diatom flora. During the study of Nova Scotian lakes, Vaughan et al. (1982) also observed that due to increased acid precipitation the diatom community structure did not respond in a linear fashion to the rapid drop in lake pH.

B. Alkaline indicator diatoms

Among the acidic lakes, Lake CS (pH 5.2) showed the highest proportion of alkaliphilous diatoms (Fig.4). This higher alkaliphilous diatom population in this lake was associated with its higher paleo-pH (Fig.14). Lake CS has recently undergone a significant decline in paleo-pH. In the surface sediment of Lake CS, the higher alkaliphilous diatom population was primarily due to the higher numbers of *Cyclotella meneghiniana* and *Fragilaria crotonensis*.

In the lakes of pH value 5.8 or higher, the alkaliphilous diatom population increased and the most alkaline lake of this study had the highest alkaliphilous diatom population (Fig.4). Among common alkaliphilous diatoms of the 28 study lakes, Cyclotella meneghiniana, Amphora ovalis, Achnanthes exigua, Fragilaria construens, F. pinnata, Nitzschia fonticola, and Cymbella angustata acted as true alkaliphilic diatoms. However, Nitzschia denticula and Achnanthes linearis can be better classified as indicators of circumneutral waters. The position of Anomoeoneis vitrea and Achnanthes exigua was uncertain (Fig.6). Although Nitzschia denticula was considered as an alkaliphilic pH indicator diatom by Merilainen (1967) and Foged (1979), in the 28 Algoma lakes, this taxon acted as a circumneutral indicator. The second alkaliphilous diatom species which acted as a circumneutral indicator was Achnanthes linearis. This taxon displayed maximum population size under circumneutral conditions. Cholnoky (1968) and Foged (1979) also reported similar observations. However, Patrick and Reimer (1966) and Merilainen (1967) considered this diatom as an alkaliphilic pH indicator.

Contrary to the findings of this study, the majority of references in Beaver (1981) considered Anomoeoneis vitrea to be an alkaliphilic diatom. However, the present study supported the explanation given by Patrick and Reimer (1966) that A. vitrea has adapted to a wide range of ecological conditions. Although Patrick and Reimer (1966), Merilainen (1967,1969), and Foged (1979) considered Achnanthes exigua as an alkaliphilic diatom, in the suface sediments of 28 Algoma lakes this taxon also showed higher population in the acidic lakes. Thus it is important to mention that in the study lakes Anomoeoneis vitrea and Achnanthes exigua acted as pH indifferent diatoms.

In my study lakes, no alkalibiontic diatoms were observed. Thus the absence of alkalibiontic diatoms from the surface sediments of the 28 Algoma lakes (pH 4.4-8.13) contradicts Hustedt's explanation that these diatoms occur at pH values above 7.0. The results of this study fit Beaver's (1981) explanation that alkalibiontic diatoms only become abundant relative to alkaliphilic forms at pH values of 9 or above.

C. Circumneutral indicator diatoms

Although no distinct pattern was observed in the distribution of circumneutral diatom populations in the 28 study lakes, their percent composition was generally higher in the circumneutral and alkaline lakes (Fig.4). The lack of pattern was probably associated with the existing discrepancies in the pH classification of these diatoms. Out of eight common circumneutral diatom taxa of the 28 study lakes, *Cyclotella comta*, *Stauroneis* spp., *Cymbella cesatii*, and *Achnanthes minutissima* were present as true circumneutral pH indicators (Fig.6). However, *Navicula radiosa*, *N. pupula*, *Cymbella minuta*, and *Nedium iridis* indicated different pH preferences than the assigned pH category (Fig.6). In the present study, *Navicula radiosa* indicated preference for both circumneutral and alkaline waters. Although Patrick and Reimer (1966) and Merilainen (1967) considered this taxon as a circumneutral diatom. The present study was in agreement with Alhonen's (1972) study. Alhonen reported that this species has no definite pH preference. Although Merilainen (1967) and Patrick (1970) considered *Navicula pupula* as a circumneutral diatom, the present study classified this taxon as an alkaliphilic diatom (Fig.6). My study indicated that at least for the Algoma lakes, Cymbella minuta should be considered as a pH indifferent rather than a circumneutral taxon. Patrick and Reimer (1975) explained that in U.S. waters Cymbella minuta is widespread at different pH. However, Cholnoky (1968) described the pH optimum of this diatom as occurring between 7.7 to 7.8. Merilainen (1967) and Foged (1979) also considered this taxon as an indicator of circumneutral waters.

In the Algoma lakes, Nedium iridis reached its highest population size at a pH around 6.0, but it was also abundant in alkaline lakes. Thus this species can be better categorized as pH indifferent. Patrick and Reimer (1966) also indicated similar observations. However, Merilainen (1967,1969) and Foged (1979) considered N. iridis as a circumneutral diatom.

Although my study gained resonable success in differentiating between the circumneutral pH indicator diatoms and the other pH indicator groups, clearly more definite autecological information is needed to improve the pH indicator status of the circumneutral diatoms.

2. Surface Sediment Diatom Species Richness Vs. Observed Lake pH

In addition to influencing the species composition and relative abundance of different pH indicator diatom groups, lake pH was also one of the most important factors affecting the diatom species richness in the surface sediments of my 28 study lakes (Fig.5). In acidic lakes (pH < 5.6), the diatom species richness was lowest while in the slightly acidic lakes (pH 5.6 to 6.5) the species richness gradually increased. The maximum number of diatom taxa were observed in the circumneutral lakes (pH 6.6 to 7.5, Fig.5). Similar to this study, Patrick (1966) and Vaughan et al. (1982) also observed maximum diatom species richness in the circumneutral lakes. Moreover, Patrick and Reimer (1966) explained that very few diatom species can live in acidic waters of pH below 3.5. Van Dam et al. (1981) also observed significant reductions in the diatom species richness at low pH in Dutch moorland pools. In comparison to circumneutral lakes, the diatom species richness was significantly lower in my alkaline lakes (Fig.5). Similar observations were reported by Patrick and Reimer (1966).

The surface sediment diatom species richness study was further extended to investigate the contribution of various pH indicator diatoms to the cumulative diatom species richness (Fig.5). The study showed that as lake pH dropped the number of acidobiontic and acidophilic diatom taxa gradually increased while the number of circumneutral and alkaliphilic diatom taxa successively decreased. The circumneutral lakes supported the maximum number of alkaliphilic and circumneutral diatom taxa, but in the alkaline lakes their numbers did not increase while the number of acid loving diatoms were greatly reduced (Fig.5). According to their pH indicator status, the pH indifferent diatoms did not show a very definite distribution pattern in the study lakes (Fig.5).

Diatom species richness in humic lakes:

Although there is a controversy about the diatom species richness in humic waters, the present study found no major variations in the diatom species richness of clearwater (sologenic) or brownwater (ombrogenic) acidic lakes. Merilainen et al. (1982) explained that increased leaching of allochthonous humic matter into a lake may result in a decrease in diatom species richness. However, they mentioned that a proportional addition of humic matter and nutrients may also cause an increase in diatom species richness. Van Dam et al. (1981) and Vaughan et al. (1982) suggested that probably due to more constant conditions associated with the brownwater acidic lakes, these lakes can support a higher number of diatom taxa than their clearwater counterparts. In this study no attempt was made to identify the humic diatom indicators. This aspect will be further studied in detail by Mr. John Ciolfi (M.Sc. thesis in prep.).

This was the first detailed study based on diatoms to demonstrate that as lake pH drops the number of diatom taxa also significantly decreases. Therefore, it can be concluded that diatom species richness and relative abundances can be sensitive indicators of lake acidification. The close relationship between surface sediment diatom assemblages and observed lake pH, greatly encouraged me to prepare a calibration curve in order to calculate the diatom inferred pH.

3. Calibration Curve

A. Significance of the index alpha calibration

Although three calibration curves (alpha, omega, and epsilon) were prepared from the surface sediment diatoms and observed lake pH (Fig.7), the relationship which was the most significant was index alpha ($r = -0.89$; $p = < 0.01$, Fig. 7). The index alpha regression line accounted for 79% of the variance between observed pH and diatom inferred pH. The relationship was less significant for index omega ($r = -0.80$; $p = <0.01$) and index epsilon ($r = 0.76$; $p = <0.01$). Furthermore the omega and epsilon regressions explained only 64% and 58% of the variance in the diatom inferred pH. When the diatom inferred pH results were compared with observed lake pH, the index alpha diatom inferred pH results were closest to the observed lake pH (Table 3). The statistically significant relationship between index alpha and the observed lake pH supports the arguments presented by Merilainen (1967), Norton et al. (1981), and Del Prete and Schofield (1981). All these researchers noted that to date, index alpha is the best available index for calculating diatom inferred pH.

Some problems associated with the use of index alpha were described by Nygaard, (1956), Merilainen (1967), Davis et al. (1980), and Norton et al. (1981). Nygaard (1956) and Merilainen (1967) noted that in strongly acidic lakes (pH $<$ 5.5), index alpha goes to infinity. They also observed that in very alkaline lakes (pH 9 or more) index alpha goes to zero. In order to avoid the extremely high index alpha results, Renberg and Hellberg (1982) included circumneutral diatoms in their modified index B.

As discussed earlier, problems were encountered during the categorization of circumneutral pH indicator diatoms of Algoma lakes, as such the index B could not be used for calculating the diatom inferred pH. Since infinity or zero index alpha results were not encountered during the study of the 28 Algoma lakes, it was possible to explain that index alpha worked well for the Algoma lakes ranging in pH from 4.40 to 8.13. In the present study, the counting of a minimum of 800 diatom frustules was necessary to provide a sufficient number of indicator diatoms for calculating a reliable index alpha. In comparison to this study, Berge (1975) counted only 200-300 diatom frustules and the number of diatom frustules (600) counted by Davis and Berge (1980) and Norton et al. (1981) were also less.

B. Problems associated with the index omega and index epsilon

The major problem which I encountered with the use of index omega and index epsilon was that these two indices did not consider both acid and alkaline diatom populations simultaneously while index alpha does. The second problem which was associated with the use of index omega and index epsilon was their over sensitivity to acid and alkaline diatom taxa identified within the sample. Merilainen (1967) also pointed out this problem. He explained that due to their sensitivity to the number of acid or alkaline taxa identified, any taxonomic error would seriously affect the final index omega or epsilon results. During the use of index omega, Berge (1975) also indicated this problem. He observed this problem specifically with the genus *Eunotia* where most of the species occur in small numbers. Many *Eunotia* species in small numbers were also identified in the low pH lakes of the present study.

Vaughan et al. (1982) indicated that the use of index omega and epsilon as an indicator of past pH excludes the possibility that a diverse diatom community could exist at low pH. They supported their argument by observing that acid humic lakes can have higher diatom species richness than would have been normally expected for an acidic lake. However, such variations were not observed in the acidic lakes of my study.

C. Variations associated with diatom inferred pH

In the present study, the pH indicator status of a number of diatom taxa was carefully defined and 800 or more diatom frustule were counted. As a result, the alpha regression equation provided an accuracy of about +/- 0.3 of a pH unit in the diatom inferred pH calculations. This error can be explained by counting errors and seasonal fluctuations in lake pH as discussed below. My observations support Berge's (1980) theory that diatom assemblages do not reflect short term pH changes. A drop in lake pH due to snow melt and heavy rains is not translated immediately into a change in diatom species composition. In addition, such short term changes are usually buffered by the buffering capacity of lake sediments (Berge 1980). Norton et al. (1981) suggested that better lake pH data would be helpful in increasing the accuracy of the diatom inferred pH technique. Since most of the study lakes were remote, this deficiency could not be corrected. However, the mid summer pH measurements were most probably free from the pH shocks such as spring snow melt and heavy rain in fall.

To increase the accuracy of the diatom inferred pH technique, Berge (1980) and Dickman (in Fortescue et al. 1981) suggested the use of only planktonic diatom species in the calculation of log alpha. Difficulties in assigning 'planktonic' versus 'benthic' status to many diatoms made this problematic. In addition, most of the planktonic diatoms disappear at pH values around 5.8 (Almer et al. 1974). Thus planktonic diatom dependent indices will not have any basis for assessing the diatom inferred pH of acidic lakes (pH <5.6). In the surface sediments of the acidic lakes, only two planktonic diatoms were present in small numbers (*Melosira distans* and *Cyclotella comta*). *Melosira distans* is an acidophilic indicator while *Cyclotella comta* is an indicator of circumneutral waters.

D. Regional differences in index alpha calibration

Since to date the index alpha is most widely used index in the diatom inferred pH studies, it is possible to compare the index alpha regression curve obtained from this study with the other 5 curves reported in the literature. Table 8 illustrates the details of individual regression equation, the correlation coefficient, the number of lakes included in the regression, the location of study area, and the reference. This information was obtained by regressing the log index alpha and observed lake pH results reported in the literature. Since the comparison was specifically done to determine the regional differences in the index alpha calibration, the lakes included from the other study areas by the authors were not included in the regression analysis. Moreover, to overcome the infinity index alpha results, the extremely acidic lakes were also excluded.

Table 8: Regression equations for the surface sediment diatom log index alpha vs. observed lake pH for the present study and the published literature.

Equation	Correlation coefficient	Number of lakes	Location	Reference
Y=6.57-0.82 log alpha	o.89	28	North of Lake Superior	This study
Y=6.68-0.74 log alpha	0.95	10	Denmark	Nygaard 1956.
Y=6.52-0.59 log alpha	0.80	24	Norway	Davis et al. In Norton et al. 1981.
Y=6.31-1.04 log alpha	0.72	07	Central New England	Del Prete & Schofield 1981.
Y=6.65-0.88 log alpha	0.95	13	Finland	Merilainen 1967.
Y=6.39-0.71 log alpha	0.78	31	Northern New England	Norton et al. 1981.

In the Algoma area, the relationship between observed lake pH and log alpha was Y = 6.57-0.82 log alpha. Where Y represents the diatom inferred pH. From the results of Table 8, it was observed that the slopes of the regression lines ranged from a low of 0.59 (Davis et al. in Norton et al. 1981) to a high of 1.04 for the Central New England lakes (Del Prete and Schofield 1981). The Y intercept ranged from a low of 6.39 (Norton et al. 1981) to a high of 6.68 (Nygaard 1956). A Student's t test was applied to compare the slopes of the regression lines (Goldstein 1964, page 144). The resulting 't' values indicated that the present study's calibration curve based on log alpha and the curves generated from the other study areas were not statistically different.

The significant relationship between surface sediment diatoms and observed lake pH strongly suggests that the diatom inferred pH technique has potential in interpreting a lake's pH history (paleo-pH). On the basis of these observations the index alpha regression equation was used for calculating the downcore diatom inferred pH of 4 selected lakes in the Algoma region. The observations of my study were similar to Del Prete and Schofield (1981), Norton et al. (1981), and Renberg and Hellberg (1982). Although there are some problems associated with the use of subfossil diatoms, to date it appears that the diatoms are one of the best indicators of lake pH.

4. Repeatability of Paleo-pH Technique

Two cores were taken from Lake W1. The downcore paleo-pH profiles of these 2 cores were compared (Fig.8). These 2 downcore pH profiles marked a very similar pH history for Lake W1. The discrepancies observed at 3 and 4 cm levels were most probably associated with the sediment focusing or compaction in the 1981 sediment core. Since the paleo-pH value of 3 cm deep sediment sample of 1981 core was close to the paleo-pH of 4 cm deep sediment sample of 1982 core, it can be suggested that in W1 Lake these two sediments were deposited at about the same time. In the 1981 sediment core the compaction could have resulted from the core sampling and/or during core extrusion. In addition, differential sediment focusing may have also occurred.

The comparison of two downcore paleo-pH profiles from Lake W1 suggested that a single sediment core taken from the deepest point in a lake provides a representative paleo pH record. The study followed a commonly accepted hypothesis that in a lake of moderate size the resuspended sediments from shallow water are usually directed towards the deepest part of the lake where they mix well with the pelagic sediments, and provide an integrated sample representing both littoral and pelagic regions (Brugam 1978; Fritz and Carlson 1982). The fall and spring turnover along with wind action are responsible factors for the movement of diatom frustules from the littoral zone to the pelagic zone and their subsequent mixing (Birks and Birks 1980). However, in a large lake, a single paleo-pH profile constructed from a single sediment core may not be necessarily representative. Round (1964) explained that lake basin size controls the diatom sequence in a sediment core, and therefore, cores taken from different parts of a lake may yield quite different diatom stratigraphy. He pointed out that in a large basin, the littoral flora is likely to be only slightly represented in the core from the centre and over-represented in cores from near the shore.

5. Study of Lake X4

A. Paleo-pH history

Due to the low buffering capacity of Lake X4 (pH 4.8; alkalinity 1.15 mg/l as $CaCO_3$; conductivity 22 μmhos/cm), major fluctuations in paleo-pH were expected. However, contrary to this, the paleo-pH profile of Lake X4 represented a stable pH history (Fig.11).

Since no paleo-pH changes were observed between the pre-*Ambrosia* and post-*Ambrosia* sediments of Lake X4, it can be speculated that the lake has been rather acidic for the last 180-200 years (Fig.11). During this period, the paleo-pH ranged around 5.0 (+/- 0.2 of a pH unit). It appears that the recent increase in acid precipitation in this area (Kerr 1982) has not caused any significant change in the lake's pH history. Moreover, for Lake X4 it is interesting to speculate that in the past, the major portion of the hydrogen ion inputs must have come from the lake's catchment area. The regional geological information compiled by Pye (1969) has indicated that the Lake X4 watershed geology is characterized by ancient acidic lava.

Coker and Shilts (1979) noted that there were localized groups of acidic lakes on the east shore of Lake Superior. They explained that the acidic conditions in many of these lakes was the result of increased acid precipitation. My results indicate that this in not true for Lake X4. Moreover, the alkalinity criterion proposed by Kerr (1982) in order to differentiate the acid sensitive lakes from the well bufferred lakes was not very useful when applied to Lake X4. Thus some caution is necessary in defining acid sensitive lakes solely on the basis of a lake's alkalinity value. Kerr (1982) emphasized that lakes with an alkalinity value of less than 10 mg/l $CaCO_3$ are extremely sensitive to increased acid precipitation. The application of paleo-pH technique would be extremely useful in differentiating the naturally acidic lakes from the lakes affected by increased acid precipitation.

B. Acid indicator diatoms in Lake X4

In the 20 cm long sediment core from Lake X4, the diatom population was basically comprised of periphytic and benthic diatoms, and no planktonic diatoms were observed. Berge (1980) also failed to find planktonic diatoms in the sediment core of his acidic lake, Lake Langtjern (Norway). He concluded that the lake was naturally acid over the last 800 years with a pH value around 5. Lake X4 displayed a similar absence of planktonic diatoms. This was also associated with its long term acidic conditions. Almer et al. (1974) observed that most of the planktonic diatoms disappeared at a pH value below 5.8.

Although the downcore paleo-pH profile of Lake X4 was constructed with the help of subfossil diatoms, it is important to discuss the downcore distribution of common pH indicator diatoms. The presence of a large acid loving diatom population in Lake X4 was a reflection of its stable acidic environment over the last 200 years (Fig.9). *Frustulia rhomboides*, which has been primarily reported from the benthic habitats (Stoermer and Yang 1969) of acidic lakes (Round 1964; Cholnoky 1968;

Merilainen 1967) was the most abundant diatom in this lake (Fig.10). In the surface sediment diatom study, this taxon was present as a true acidophilic diatom with an optimum population at pH 4.4 to 6.4 (Fig.6). The second and third most abundant diatoms in Lake X4 were Eunotia spp. and Anomoeoneis serians var. brachysira (Fig.10). Foged (1954) and Round (1964) explained that most of the Eunotia species prefer acidic conditions. This was confirmed in the surface sediments of 28 Algoma lakes. Kwiatkoski and Roff (1976) and Norton et al. (1981) demonstrated that the majority of Eunotia spp. show optimum population maxima at a pH between 4.5 and 6.1. The third most abundant diatom in Lake X4, Anomoeoneis serians var. brachysira also requires acidic conditions for optimum growth (Merilainen 1967; Foged 1979; Norton et al. 1981).

In the top two centimeters of sediments, Tabellaria binalis population abruptly increased in Lake X4 while the population of Semiorbis hemicyclus did not increase (Fig.10). Although no significant paleo-pH changes were observed in Lake X4 (Fig.11), a slight decrease in pH in the top 2 cm of this core was associated with an increase in the T. binalis population. During the study of 24 SNSF lakes, Davis and Berge (1980) observed that the maximum abundance of S. hemicyclus and T. binalis occurred at a pH between 4.4 to 5.1. Berge (1980) categorized these two diatoms as very useful pH indicators. In the surface sediment diatom study of my 28 lakes, these two taxa were present as true acidobiontic diatoms (Fig.6).

Although the paleo-pH of Lake X4 was near the optimum for acidobiontic diatoms (<5.5), their population size in this lake never exceeded more than 15% of its total (Fig.9). However, in comparison to the other three lakes which I studied for downcore paleo-pH (Figs.12,15, and 18), the acidobiontic diatom population in Lake X4 was high.

Due to a stable acidic environment, the alkaline diatom population did not thrive in Lake X4 (Fig.9). The circumneutral diatom population in Lake X4 remained very stable between 2 to 20 cm. Their percent composition suddenly increased at the surface of the core (0-2 cm) (Fig.9). This increase in circumneutral diatoms was mainly attributed to the higher numbers of _Nitzschia palea_ (Fig.10). Although Foged (1974), Merilainen (1967; 1970) and Nygaard (1956) considered _N. palea_ as a circumneutral diatom, their higher population in the surface sediments of Lake X4 can not be easily explained. Since _N. palea_ is a very tolerant freshwater diatom usually abundant in organically polluted waters (Patrick 1970), some nutrient related factor may have been responsible for its increase in the surface sediment. However, no cottage development has occurred on or near Lake X4. Although it is quite speculative, Dickman (in Fortescue et al. 1983) has pointed to increased beaver activity in some Algoma lakes as a potential nutrient source. In Lake X4, the beaver activity was evident near the lake's outlet and water level seemed to be lowered about one meter from its original mark.

6. Study of Lake CS

A. Paleo-pH history

On the basis of Kerr's (1982) alkalinity criterion, Lake CS (alkalinity 1.56 mg/l as $CaCO_3$) can be categoriged as an extremely sensitive lake in terms of acid precipitation. As expected through the preliminary water survey results, the paleo-pH of Lake CS has significantly dropped over the last 30 years (Fig.14) Since circa 1954, the lake's paleo-pH has declined from 7.1 to 6.4. Although its paleo-pH dropped 0.7 of a pH unit, drop in pH is even greater if the paleo-pH value of circa 1954 is compared with the 1982 observed lake pH of 5.2. From this latter comparison it appears that over the last 30 years the pH of Lake CS has dropped almost 2 full pH units. In contrast, between circa 1890 and 1954 the paleo-pH of Lake CS remained very stable (pH 7.1-7.3, Fig.14).

As noted above, there was a big discrepancy between the surface sediment diatom inferred pH of Lake CS (6.2) and the observed lake pH (5.2). The discrepancy was most probably due to the time required for the replacement of alkaliphilic and circumneutral diatoms by the acidophilic and acidobiontic diatom population as a lake acidifies. A similar hypothesis was also proposed by Del Prete and Schofield (1981) for Lake Honnedaga, New England. Their observed lake pH and diatom inferred pH were 4.7 and 5.6 respectively. Lake Honnedaga was the only lake in their study area undergoing rapid acidification. In Lake CS, the rapid decrease in diatom inferred pH was probably associated with its poor buffering. The pH of most waters moves rather slowly towards a value approaching pH 6.0, but below this pH the bicarbonates are replaced by sulfate and carbon dioxide and once this happens pH drops rapidly (Wright and Gjessing 1976; Dickman in Fortescue et al. 1981). On the basis of this hypothesis it is possible to explain that in the begining when water pH was dropping slowly in Lake CS the diatoms responded accordingly, but later when the bicarbonates were exhausted, the lake pH dropped rapidly and hence did not provide sufficient time for the diatom shift from circumneutral to acid species. To date, virtually no definite information is available to explain the lag period required for the shift in diatom populations, subsequent to increased acid precipitation. However, to some extent this information can be provided by the lake liming study done by Renberg and Hellberg (1982) on Lake Lysevatten (Sweden). They increased its pH from 4.7 to 7.1 over a two year period. Their observations indicated that after liming the lake, the diatom flora showed a gradual shift, but did not come to the level expected for pH 7.1.

B. Causes of lake acidification

From the Lake CS paleo-pH study a question of great interest comes to the fore; "what has caused the rapid decrease in lake pH over the past 30 years". Coker and Shilts (1979) and Kerr (1982) indicated that increased acid precipitation was the major factor responsible for the recent pH decline in a number of Algoma lakes. In the Algoma District the increased acid precipitation has been identified as both local and long range (Coker and Shilts 1979). Locally the Algoma sintering plant which is located approximately 24 km south east of Lake CS emits about 141,000 tonnes of sulfur dioxide every year (Dept. of Envirn. 1981). For long range sources, Coker and Shilts (1979) and Shannon and Voldner (1982) reported that significant amounts of sulfur dioxide are transported from the northeastern United States, particularly from the Ohio valley and the Midwest. Therefore, on the basis of the literature, it can be suggested that the increased acid precipitation is the most probable factor responsible for the recent pH decline in Lake CS.

C. Lake oligotrophication

Along with the decrease in lake pH, the subfossil diatom population also indicated that Lake CS was becoming more oligotrophic. In the upper portion of the core (0-5 cm), the eutrophic or mesotrophic diatom population represented by *Cyclotella meneghiniana* and *Fragilaria construens*, greatly declined. At the same time those diatoms which are assciated with mesotrophic to oligotrophic conditions (*Cyclotella comta*, *Eunotia* spp., *Frustulia rhomboides*, *Anomoeoneis serians* var. *brachysira*) increased rapidly (Fig.13). Thus the diatom stratigraphy suggested that originally Lake CS was more nutrient rich. Granberg (1972) considered that in general the alkaliphilous diatom species are eutrophic indicators while the acidophilous diatoms are an indicator of oligotrophy. Although the percent composition of *Cyclotella comta* increased detectably from 4.5 to 2.5 cm core depth, their population again declined slightly in the upper 2.5 cm of sediments. The decrease in *C. comta* population was most probably associated with its higher pH preference. Figures 12 and 13 illustrated that in the upper portion of the core the alkaliphilic diatom population gradually declined while the acidobiontic and acidophilic diatom population increased. Although *Fragilaria crotonensis* is associated with mesotrophic to eutrophic waters, no significant changes were observed in the downcore distribution of this species (Fig.13). The reasons associated with their higher population will be discussed later.

In Lake CS, oligotrophication has probably resulted from its rapid acidification. Gorham (1976) and Grahn et al. (1974) explained that increaesd acid precipitation may lead to lake acidification and consequently oligotrophication. Moreover, this kind of lake oligotrophication acts as a feedback mechanism and accelerates the process of acidification (Grahn et al. 1974). Renberg and Hellberg (1982) explained that in areas of crystalline bedrock and nutrient poor soil types the inputs of nutrients decrease with time. This natural process can be accelerated by inputs of acidic substances.

D. Lake acidification and eutrophication

Lake acidification and subsequent oligotrophication is not a universal phenomenon (Van Dam and Blokland 1978; Van Dam et al. 1981). If in the future, Lake CS continues to decrease in pH, the lake may actually become eutrophic. Since the solubility of phosphorus increases when the pH drops below 5.0, Van Dam and Blockland (1978) conclude that in time lake acidification will lead to eutrophication. They supported their explanation by observing an increase in eutrophic diatoms (eg. *Cyclotella meneghiniana* and *Cocconeis placentula*) by comparing them to samples collected in 1920 and 1978. However, since the eutrophic diatom species have rather high pH optima, they were present in very low numbers (Van Dam et al. 1981).

E. Downcore changes in species composition

The recent diatom population changes of Lake CS were mainly quantitative while only minor qualitative changes occurred. In the upper portion of the core, the increase in acidophilic diatoms was mainly attributed to the higher numbers of *Anomoeoneis serians* var. *brachysira*, *Eunotia* spp., *Frustulia rhomboides*, and *Tabellaria fenestrata* (Fig.13). As indicated by the surface sediment diatom analysis of 28 study lakes all these acidophilic diatom taxa have specific preference for acidic lake environments (Fig.6).

In the top 2.5 cm of sediments an increase in acidobiontic diatom population was associated with an increase in the relative abundance of acidobiontic diatoms and not the invasion of new acidobiontic diatom species. As the lake became increasingly acidic, the *Actinella punctata* population successively increased. This indicates that *A. punctata* has slightly higher pH optimum than the other acidobiontic diatoms. This explanation can be equally supported by the surface sediment diatom results (Fig.6). In the surface sediments of 28 lakes, *A. punctata* was present at slightly higher pH than were the other common acidobiontic diatoms (*Semiorbis hemicyclus*, *Anomoeoneis serians*, and *Tabellaria binalis*, Fig.6).

In the upper portion of the sediment core (0-5 cm), the decrease in alkaliphilous diatoms was primarily associated with the decrease in Cyclotella meneghiniana and Fragilaria construens (Fig.13). In Lake CS, C. meneghiniana was the most abundant diatom. Although this taxon is a common indicator of alkaline waters (Cholnoky 1968; Foged 1979; Sparling and Nalewajko 1970), in small lakes this taxon usually represents an eutrophic environment (Bradbury 1975; Stoermer and Yang 1970). Cyclotella meneghiniana can be found in mesotrophic lakes, but rarely occurs in oligotrophic waters (Stoermer et al. 1971). With regards to its habitat, C. meneghiniana has been considered as benthic, epipelic, and tychoplanktonic. It has also been referred to as euplanktonic (Cholnoky 1968). Similar to C. meneghiniana, Fragilaria construens also decreased in numbers in the upper portion of the core (Fig.13). Fragilaria construens has been widely documented as an alkaliphilic diatom (Patrick and Reimer 1966; Cholnoky 1968; Foged 1979). In the surface sediment diatom analysis this taxon was mainly present in the circumneutral and alkaline lakes (Fig.6). Stoermer and Yang (1969) explained that F. construens reached its maximum abundance in eutrophic lakes and Patrick and Reimer (1966) and Kling and Holmgren (1972) explained that this taxon commonly occurs in benthic and planktonic zones of mesotrophic to eutrophic waters. Contrary to the distribution of C. meneghiniana and F. construens, the downcore distribution of F. crotonensis in Lake CS remained very constant (Fig.13). Although F. crotonensis commonly occurs in moderately alkaline lakes (Duthie and Rani 1967; Round 1964), Schofield and Galloway (1977) observed this taxon in the pH range 5.1 to 5.3. Similar to observations reported by Schofield and Galloway (1977), the present study indicated that *F. crotonensis* can maintain its population even under acid stressed conditions. Patrick and Reimer (1966) explained that *F. crotonensis* is a planktonic species widely distributed in mesotrophic waters.

Along with the increase in acidophilous diatoms observed in Lake CS, the circumneutral diatom population also increased in the upper portion of the core (Fig.12). This increase was primarily associated with the increase in *Cyclotella comta* (Fig.13). *C. comta* has been commonly considered as an circumneutral pH indicator diatom (Patrick 1970; Sparling and Nalewajko 1970). *Cyclotella comta* is an euplanktonic diatom (Round 1957) and has been commonly reported from oligotrophic to mesotrophic waters (Hutchinson 1967; Stoermer and Yang 1970).

F. Acidification of Lake CS

From the study of downcore diatom inferred pH and the composition of various pH indicator diatom groups it is obvious that Lake CS is shifting towards more acidic and more oligotrophic conditions. Prior to circa 1954, the lake was circumneutral, but since 1954, the acid loving diatom population has gradually increased due to decreased lake pH (observed pH 5.2). On the basis of published information it is possible to speculate that the increased acid precipitation is the most probable factor for the observed drop in lake pH.

7. Study of Lake U3

A. Paleo-pH history

In comparison to CS and X4 lakes, Lake U3 was well buffered (pH 7.05; alkalinity 16.6 mg/l as $CaCO_3$; conductivity 60 µmhos/cm). On the basis of Kerr's (1982) alkalinity criterion the lake can be categorized as not particularly sensitive to increased acid inputs. My paleo-pH study indicated that Lake U3 was characterized by a relatively stable environment over the past 100-140 years with a diatom inferred pH range between 6.9 and 7.2 (Fig.17).

As Lake U3 is located only about 9 km north of Lake CS, a similar precipitation chemistry can be expected for both lakes. As expected, the downcore paleo-pH profiles of these two lakes indicated very similar paleo-pH results (+/- 0.2 pH units) for the sediments accumulated prior to circa 1954 (Figs.14 and 17). However, in these two lakes major paleo-pH variations were observed in the recent period (post circa 1954). The paleo-pH profile of Lake U3 remained very stable after 1954, while the paleo-pH of Lake CS dropped significantly. The stable paleo-pH profile of Lake U3 indicated that the well bufferred Lake U3 neutralized the increased hydrogen ion inputs while Lake CS could not (pH 5.2; alkalinity 1.56 mg/l as $CaCO_3$; conductivity 46 µmhos/cm). Moreover, the large surface (0.58 km^2) and watershed area (4.25 km^2) of Lake U3, probably provided enough buffering capacity to neutralize the increased acid inputs. However, due to smaller surface

(0.09 km^2) and watershed area (1.8 km^2), Lake CS started loosing its buffering power roughly 30 years ago. Dillon et al. (1978) and Groterud (1981) explained that lakes with smaller surface and watershed areas are more sensitive to increased acid precipitation.

B. Downcore changes in species composition

In Lake U3, no major fluctuations were observed in the downcore distribution of common pH indicator diatoms (Fig.15). The diatom flora was typically alkaliphilic to circumneutral with relatively small populations of acidophilic diatoms. In this lake the higher numbers of alkaliphilic diatoms were primarily due to larger populations of *Melosira granulata*, *Fragilaria construens*, *F. pinnata*, *Cyclotella bodanica*, and *Cyclotella meneghiniana* (Fig.16). *M. granulata* and *F. construens* were the two most abundant alkaliphilic diatoms in the lake. *Melosira granulata* is a planktonic diatom and has been commonly reported from eutrophic (Stoermer and Yang 1969,1970; Bradbury 1975) alkaline waters (Round 1964; Patrick 1970). *Fragilaria construens* is also an indicator of eutrophic to mesotrophic alkaline waters (Stoermer and Yang 1969; Patrick 1970; Kling and Holmgren 1972). Moreover, the majority of other common diatom taxa in Lake U3 (*Tabellaria fenestrata*, *Melosira distans*, *Cyclotella meneghiniana*, and *Fragilaria pinnata*) were also indicators of mesotrophic to eutrophic conditions.

8. Study of Lake W1

A. Paleo-pH history

Lake W1 is located within the fume kill area of the Algoma sintering plant. Despite its location, the surface water pH (6.66), alkalinity (13.26 mg/l as $CaCO_3$), and conductivity (79 μmhos/cm) indicate that the lake is not very sensitive to acid precipitation. The carbonate-rich (siderite, Fe_2CO_3) bedrock geology of Lake W1 has probably provided enough buffering to neutralize the increased hydrogen ion inputs entering this lake since the commencement of iron smelting and sintering in the Wawa area.

In contrast with the paleo-pH study of other neutral pH lakes (Lake U3), the downcore paleo-pH profile of Lake W1 indicated major fluctuations in paleo-pH (Fig.20). Over the last 150 years, diatom inferred pH in Lake W1 has ranged between 7.1 and 8.0. The lake's paleo-pH remained fairly stable (7.1-7.4) between circa 1890 and 1936, but since about 1936, the paleo-pH has fluctuated widely. These paleo-pH fluctuations were most probably associated with the increased watershed activities.

Between circa 1936 and 1957, the paleo-pH significantly increased from 7.4 to 8.0 (Fig.20). Since frequent forest fires have been reported in the fume kill area (Donnelly and Harington 1978 in Fortescue et al. 1983), these forest fires could be one reason for the increase in lake pH. The mechanism responsible for increasing lake pH following a forest fire was discussed in detail by Dickman (in Fortescue et al. 1983). He indicated that forest fires alter the litter layer and subsequently effects the ion binding power of the deeper leaching layers in the forest floor. This disturbance can result in a release of carbonates from the leached layers and subsequently an increase in lake pH until a new equilibrium is established. Moreover, Dickman hypothesized that due to forest fire there would be an influx of nutrients into the lake. This would result in an increase in aquatic plant and algal growth which subsequently increases lake pH as more carbon dioxide and the carbonic acid is removed from the water by these plants. Likens and Bormann (1974) also explained that watershed activities such as forest fires and logging events can result in increased inputs of dissolved and particulate matter enhancing their rate of eutrophication. This eutrophication can in turn cause an increase in lake pH (Likens and Bormann 1974). Although these two studies indicated that a forest fire can result in increased lake pH, the effects of forest fires on lakes are still controversial. Schindler et al. (1980) studied the effects of a forest fire on an E.L.A. watershed. They reported significant losses of nitrogen, phosphorus, and potassium from a Precambrian watershed, but in the nearby Lake Rawson, the phytoplankton and nutrient concentrations were not increased detectably. However, they pointed out that due to long water renewal times for Lake Rawson (about 7 years), the forest fire effects may occur after several years. Stockner (1971) also failed to observe any detectable effect of forest fire on the diatom flora of Experimental Lake 240.

While explaining a possible mechanism responsible for pH increase in Lake W1 between circa 1936 and 1957, it is important to mention the lake alkalization study done by Kilham (1982). During the study of

Weber Lake in Michigan, he observed that within a well bufferred area, the increased acid precipitation can lead to lake alkalization. This was mainly due to enhanced rates of carbonate weathering in the drainage area. Within the past 30 years the pH of Weber Lake increased from 6.6 to about 7.7. Since in the fume kill area the precipitation became increasingly acidic after the extension of the Wawa sintering plant in 1949 (Gordon and Gorham 1963), the increase in lake pH prior to 1949 can not be explained by the Weber Lake study.

In Lake W1, the second significant paleo-pH shift occurred between circa 1957 and 1970 (Fig.20). Within this period the paleo-pH dropped from 8.0 to 7.1. In order to correlate this paleo-pH decrease with watershed activities it is tempting to speculate that the drop in lake pH was most probably associated with the extension of the Algoma sintering plant in 1949 (Gordon and Gorham 1963). Similarly although the sintering plant started up operation in the early nineteenth century, there was extensive vegetation damage resulting from the fume kill after the extension of the plant in 1949 (Gordon and Gorham 1963). The paleo-pH decrease was closly mirrored by the elevated levels of downcore iron and manganese in Lake W1 sediments as reported by Fortescue et al. (1983). These higher levels of iron and manganese in the core were associated with the fallout from the Algoma sintering plant. Fortescue et al. (1983) also explained that in comparison to sodium, the levels of potassium were also higher in the post-*Ambrosia* sediment of Lake W1, suggesting an increase in secondary minerals associated with the defoliation of the catchment area by the fume kill.

Between circa 1970 and 1974, the Lake W1 paleo-pH significantly increased from a low of 7.1 to a high of 8.0 (Fig.20). Since within this period no significant reductions were reported from the Algoma sintering plant, the paleo-pH increase may be associated with the increases in alkaline fly ash to the lake from the smelter (Thode and Dickman 1983). Thode and Dickman (1983) indicated that lakes which are downwind of the Algoma sintering plant receive considerable amounts of fly ash along with the emissoins of sulfur dioxide. In addition to fly ash, a similar kind of mechanism may also be responsible for the increase in lake pH as explained for the sediments accumulated between circa 1936 and 1957. It is important to mention that although between 1970 and 1974 the paleo-pH increased in a similar manner as increased between 1936 and 1957, the increase was much more rapid between circa 1970 and 1974. Between 1936 and 1957 (21 years) the paleo-pH increased 0.6 of a pH unit, while between 1970 and 1974 (4 years) the paleo-pH increased 0.9 of a pH unit. The rapid paleo-pH increase between 1970 and 1974 indicated that the factor or factors responsible for this increase had a greater impact than the one responsible for the paleo-pH increase between 1936 and 1957.

The paleo-pH of circa 1974 significantly decreased towards the surface of the core (Fig.20). Since 1974 the Lake W1 paleo-pH dropped at approximately 0.1 of a pH unit every year. The recent pH decrease was most probably associated with the sulfur dioxide emissions of the Algoma sintering plant. The present sulfur dioxide emission levels of this plant are 141,000 tonnes each year (Govt. of Canada 1981). These levels are significantly higher than the 100,000 tonnes/year reported in 1960 by Gordon and Gorham (1963).

In Lake W1, the recent paleo-pH decline rates are very similar to McNicol's (1980) study. He explained that within the well buffered fume kill area the lakes are loosing their pH at an average rate of 0.09 to 0.10 pH unit every year. Although within the fume kill area the precipitation chemistry is highly acidic, the slow pH decrease can be explained by the hypotheses proposed by Kramer (1975) and Thode and Dickman (1983). Kramer (1975) explained that calcareous surficial sediments and/or bedrock lithologies can assimilate excessive hydrogen ions and therefore, can continue to buffer the local waters. With reference to lakes located in the fume kill area, Thode and Dickman (1983) explained that sintering of siderite releases a fine limestone ash (sinter flux) into the atmosphere which helps to counteract the impact of sulfur dioxide which is released at the same time.

B. Downcore changes in species composition

In Lake W1, the downcore diatom population also fluctuated widely (Figs.18 and 19). Although most of the major diatom species were encountered at different depths, over the past 30 years their relative abundance varied enormously (Fig.19). The major variations were observed between the surface and seven centimeters. The calculated paleo-pH shift between circa 1936 and 1957 (Fig.20) was due to a slight decrease in acidophilous diatom population and the abrupt increase in alkaliphilous diatoms (Fig.18). The increase in the alkaliphilous diatom population was associated with the higher numbers of Achnanthes linearis and Fragilaria pinnata (Fig.19). A. linearis usually occurs in periphytic communities of lakes (Stoermer and Yang 1969) displaying a range of pH between 6.5 to 8.5 (Patrick and Reimer 1966). *Fragilaria pinnata* also commonly occurs in the periphytic communities of freshwaters (Round 1957; Patrick and Reimer 1966), but this taxon has relatively narrow pH optima (7.6-7.8) (Cholnoky 1968). These two diatom taxa were also responsible for the decrease in alkaliphilous diatom populations between the 3 cm and the surface sediments (Fig.18). Thus on the basis of available ecological information it is possible to explain that due to their higher pH optimum, *A. linearis* and *F. pinnata* population abruptly increased when the water pH increased in Lake W1.

The significant paleo-pH decrease between circa 1957 and 1970 (Fig.20) resulted in a slight increase in acidophilous diatoms and a major decrease in alkaliphilous diatoms (Fig.18). The major portion of the decreasing alkaliphilous diatom population was closely mirrored by an increase in circumneutral diatoms (Figs.18 and 19). When in the past the lake pH shifted from slightly alkaline to neutral, the circumneutral diatom population successively increased and vice versa. The circumneutral diatom population increase was primarily due to higher numbers of *Cymbella cesatii*, *C. minuta*, *Navicula radiosa* var. parva, *N. pupula* var. *rectangularis*, and *N. peregrina* (Fig.19). The paleo-pH increase between circa 1970 and 1974 and the paleo-pH decrease between circa 1974 and 1982 (Fig.20) were also closely related to variations in the alkaliphilous and acidophilous diatom populations (Fig.18). Although circumneutral diatoms were not included in the paleo-pH calculations of Lake W1, their populations were monitored. They too fluctuated greatly in the lake over the last 30 years.

CONCLUSIONS

1. The surface sediment diatom analysis of 28 Algoma Lakes indicated that pH was one of the most important factors affecting the relative abundance and species composition of their diatom populations. Along with the drop in lake pH the number of diatom taxa also significantly decreased. Therefore, the diatom community organization and species richness can be sensitive indicators of lake acidification. My findings are similar to those of Merilainen (1967), Del Prete and Schofield (1981), and Norton et al. (1981). Each of these authors concluded that diatoms are useful indicators of lake pH.

2. More definitive autecological information is needed to refine the pH indicator status of circumneutral diatoms.

3. The absence of alkalibiontic diatoms from the surface sediments of the 28 study lakes (pH 4.4 to 8.13) indicated that these diatoms require more alkaline water than explained by Hustedt (1938).

4. To date the index alpha is the best available index for calculating the diatom inferred pH, as long as sufficient numbers of diatom frustules (800-1,000) are accurately identified and counted.

5. My comparison of the index alpha calibration curve and those reported from 5 other study areas failed to show any statistically significant differences between these regression lines.

6. The comparison of two paleo-pH profiles of Lake W1 confirmed that the downcore paleo-pH technique is repeatable.

7. The paleo-pH study of Lake X4 demonstrated that over the last 200 years, the lake has been rather acidic (pH 4.9-5.2). It appears that the recent increase in acid precipitation has not caused any significant change in the lake's pH.

8. Lake U3 was characterized by a stable environment for the last 100-140 years, with a diatom inferred pH range between 6.9 and 7.2. The lake is sufficiently buffered to neutralize recent increases in acid inputs.

9. Lake W1 has undergone major fluctuations in pH over the last 50 years. These were most probably associated with increased sulfur dioxide emissions from the Algoma sintering plant and the frequent forest fires in the fume kill area.

10. Over the last 30 years, the pH of Lake CS has dropped from 7.1 to 5.2. On the basis of published information it is possible to indicate that an increased level of acid precipitation during the last 30 years is the most probable factor responsible for the recent decline in pH of this lake.

11. Paleo-pH technique appears to permit the differentiation between naturally acidic lakes and lakes affected by anthropogenic acid precipitation.

LITERATURE CITED

Altshuller, A.P. and G.A. McBean. 1979. The LRTAP problem in North America: A priliminary overview. Report of the United States-Canada Research Consultation Group on the Long Range Transport of Air Pollutants, U.S Environmental Protection Agency, North Carolina.

Alhonen, P. 1972. The geological development and paleolimnology of a small polluted lake in S. Finland. Comment. Biol. 57: 1-34.

Almer, B.W., W. Dickson, C. Ekstrom, E. Hornstrom and V. Miller. 1974. Effects of acidification on Swedish lakes. Ambio. 3: 30-36.

Babich, H., D.L. Davis and G. Stotzky. 1980. Acid precipitation - causes and cansequences. Environment. 32: 6-13 and 30-36.

Battarbee, R.W. 1973. A new method for the estimation of absolute microfossil numbers, with special reference to diatoms. Limnol. Oceanogr. 18: 647-653.

Beamish, R.J. 1974. The loss of fish population from unexploited remote lakes in Ontario, Canada as consequence of atmospheric fallout of acid. Wat. Res. 8: 85-95.

Beamish, R.J. 1976. Acidification of lakes in Canada by acid precipitation and resulting effects on fishes. Water, Air and Soil Pollution. 6: 501-514.

Beamish, R.J. and H.H. Harvey. 1972. Acidification of the LaCloche Mountain lakes, Ontario and resulting fish mortalities. J. Fish. Res. Bd. Can. 29: 1131-1143.

Beamish, R.J., W.L. Lockhart, J.C. VanLoon and H.H. Harvey. 1975. Longterm acidification of lakes and resulting effects on fishes. Ambio. 4: 98-102.

Beaver, J. 1981. Apparent ecological characteristics of some common freshwater diatoms. Ontario Ministry of Environment, Ontario. 517 pp.

Berge, F. 1975. pH changes and sedimentation of diatoms in Lake Langtjern, Norway. SNSF Internal Report, IR 11/75. 11 pp.

Berge, F. 1980. Diatoms and pH in some lakes in the Adger and Hordaland Counties, Norway. SNSF Internal Report, IR 42/79. 64 pp.

Birks, H.J.B. and H.H. Birks. 1980. Quaternary Paleoecology. University Press. Baltimore. 389 pp.

Boissonneau, A.N. 1966. Glacial history of northeastern Ontario, I. The Cochrane - Hearst area. Can. J. of Earth Sci. 3: 559-578.

Bradbury, J.P. 1975. Diatom stratigraphy and human settlement in Minnesota. Geol. Soc. Spec. Pap. 171. 74 pp.

Bradbury, J.P. and T.C Winter. 1976. A real distribution and stratigraphy of diatoms in the sediments of Lake Sallie, Minnesota. Ecology. 57: 1005-1014.

Brugam, R.B. 1978. Human disturbance and the historical development of Linsley Pond. Ecology. 59: 19-36.

Cholnoky, F.J. 1968. The Ecology of Diatoms in Inland Water. J. Cramer. Lehre. 699 pp.

Ciolfi, J. (in prep.). A comparison between the diatom inferred pH changes in brownwater and clearwater lakes. M.Sc. Thesis. Brock University.

Cleve-Euler, A. 1951-1955. Die Diatomeen von Schweden und Findland. Kunglia Svenska Velenskapsakademien Avhandlingar. Ser. 4: 961 pp.

Coker, W.B. and W.W. Shilts. 1979. Lacustrine geochemistry around the north shore of Lake Superior: implications for evaluation of the effectes of acid precipitation. Geol. Servey of Canada. 79: 1-15.

Cronan, C.S. and C.L. Schofield. 1979. Aluminum leaching response to acid precipitation: effects on high-elevation watersheds in the northeast. Science. 204: 304-306.

Davis, R.B. and F. Berge. 1980. Atmospheric deposition in Norway during the last 300 years as recorded in SNSF lake sediment, Part II: Diatom stratigraphy and inferred pH. SNSF Report. 11 pp.

Davis, R.B., M.O. Smith, J.H. Bailey and S.A. Norton. 1978. Acidification of Maine (USA) lakes by acid precipitation. Verh. Internat. Verein. Limnol. 20: 532-537.

Davis, R.B., S.A. Norton, D.F. Brakke, F. Berge and T. Hess.1980. Atmospheric deposition in Norway during the last 300 years as recorded in S.N.S.F. lakes sediments. Part IV. Synthesis, and comparison with New England lakes. S.N.S.F. Report. 2 pp.

Del Prete, A. and C. Schofield. 1981. The utility of diatom analysis of lake sediments for evaluating the acid precipitation effects on dilute lakes. Arch. Hydrobiol. 91: 333-340.

Dickman, M., S. Dixit, J. Fortescue, J. Terasmae and R. Barlow. 1983. Diatoms as indicators of lake acidification. Water, Air and Soil Pollution. (in press).

Dickson, W. 1978. Some effects of acidification on Swedish lakes. Verh. Internat. Verein. Limnol. 20: 851-856.

Digerfeldt, G. 1972. The post-glacial development of Lake Trummen. Folia. Limnol. Scand. 16: 1-140.

Dillon, P.J., D.S. Jeffries, W. Snyder, R. Reid, N.D. Yan, D. Evens, J. Moss and W.A. Scheider. 1978. Acidic precipitation in south-central Ontario: Recent observations. J. Fish. Res. Bd. Can. 35: 809-815.

Dillon, P.J., N.D. Yan, W.A. Scheider and N. Conroy. 1979. Acidic lakes in Ontario, Canada: Characterization, extent, and responses to base and nutrient additions. Archiv. Hydrobiol. 13: 317-336.

Duthie, H.C. and R.G.M. Rani. 1967. Diatom assemblages from pleistocene inter-glacial beds at Toronto, Ontario. Can. J. Bot. 45: 2249-2261.

Foged, N. 1954. On the diatom flora of some Funen lakes. Folia Limnol. Scan. 6: 1-75.

Foged, N. 1974. Freshwater diatoms in Iceland. Biblitheca Phycologia. 15: 191 pp.

Foged, N. 1979. Diatoms in New Zealand, the North Island. J. Cramer. Hirschberg, Germany. 225 pp.

Fortescue, J.A.C., I. Thomson, M. Dickman and J. Terasmae. 1981. Multidisciplinary followup of regional pH patterns in lakes north of Lake Superior, District Algoma (Part 1). Ont. Geol. Survey, Open File Report 5342. 122 pp.

Fortescue. J.A.C., R. Barlow, M. Dickman, J. Terasmae and D. Wadge. 1983. Multidisplinary followup of pH observations in lakes north and east of Lake Superior. Ont. Geol. Survey. Open File Report (in prep.).

Frey, D.G. 1969. The rationale of paleolimnology. Mitt. Internat. Verein. Limnol. 17: 7-18.

Frey, D.G. 1974. Paleolimnology. Mitt. internat. Verein. Limnol. 20: 95-123.

Fritz, S.C. and R. E. Carlson. 1982. Stratigraphic diatom and chemical evidence for acid strip-mine lake recovary. Water, Air and Soil Pollution. 17: 151-163.

Gerloff, J. and B.J. Cholnoky. 1970. Diatomaceae II. J. Cramer, Hirschberg, Germany. 835 pp.

Germain, H. 1981. Flore Des Diatomees. Societe Nouvelle Des Editions Boubee, Paris. 444 pp.

Gjessing, E.T., A. Henriksen, M. Johannessen and R. F. Wright. 1976. Effects of acid precipitation on freshwater chemistry. In Braekke, F.H. (ed.). Impact of acid precipitation on forest and freshwater ecosystems in Norway. SNSF Project, F.R. 6/76: 65-86.

Goldstein, A. 1964. Biostatistics, An Introductory Text. MacMillan. New York. 272 pp.

Gordon, A.G. and E. Gorham. 1963. Ecological aspects of air pollution from an iron-sintering plant at Wawa, Ontario. Can. J. Bot. 41: 1036-1078.

Gorham, E. 1958. The influence and importance of daily weather conditions in the supply of chloride, sulphate, and other ions to fresh waters from atmospheric precipitation. Phil. Trans. Royal. Soc. London. B: 147-241.

Gorham, E. 1976. Acid precipitation and the influence on aquatic ecosystems - an overview. Water, Air and Soil Pollution. 6: 457-481.

Gorham, E. and A.G. Gordon. 1960. The influence of smelter fumes upon the chemical composition of lake waters near Sudbury, Ontario, and upon the surrounding vegetation. Can. J. Bot. 38: 477-487.

Gorham, E. and W.W. McFee. 1980. Effects of acid deposition upon outputs from terristrial to aquatic ecosystems. In Hutchinson, T.C. and M. Havas (eds.). Effects of acid precipitation on terristrial ecosystems. Plenum Press, New York: 465-480.

Government of Canada. 1981. Stillwaters, the chilling reality of acid rain. A report by the sub-committee on acid rain. Ottawa, Canada.

Grahn, O., H. Hultberg and L. Landner. 1974. Oligotrophication - a self accelerating process in lakes subjected to excessive supply of acid substances. Ambio. 3: 93-94.

Granberg, K. 1972. The diatom successions in recent sediments and the eutrophication of Ristiselka, Lake Paijanne, central Finland. Aqua. Finnia: 20-27.

Groterud, O. 1981. The dynamics of acidification from a new view elucidated by studies in a lake area in Norway. Verh. Internat. Verein. Limnol. 21: 406-411.

Harvey, H.H. 1975. Fish population in a large group of acid stressed lakes. Verh. Internat. Verein. Limnol. 19: 2406-2417.

Henriksen, A. and R.F. Wright. 1978. Concentrations of heavy metals in small Norweigian lakes. Water Research. 12: 101-112.

Holt, R. and R. Winston. 1962. Morphology and Evolution of Fossil Plants. Rinehart and Winston. New York. 189 pp.

Huber - Pestalozzi. 1942. Das Phytoplankton des Susswassers. Unuerandereter Nachdruck, Stuttgart. 549 pp.

Hustedt, F. 1930. Bacillariophyta (Diatomea), in Pascher, A. (ed.). Die Susswasserflora Mitteleuropas. Jena. 10: 446 pp.

Hustedt, F. 1938. Systematsche und okologische Untersuchungen uber die Diatomeen- Flora von Java, Bali und Sumatra. Archiv. Hydrobiologie Suppl. 16: 1-155, 274-394.

Hutchinson, G.E. 1967. A Treatise on Limnology. Volume ii. John Wiley and Sons Inc. New York. 1115 pp.

Kerr, S.J. 1982. Impact of acidic precipitation on the sport fisheries and water quality of surface water bodies near Wawa, Ontario. Draft Report, Ontario Ministry of Natural Resources. 62 pp.

Kilham, P. 1982. Acid precipitation: its role in the alkalization of a lake in Michigan. Limnol. Oceanogr. 27: 856-867.

Kling, H. J. and S.K. Holmgren. 1972. Species composition and seasonal distribution of phytoplankton in the Experimental Lakes Area, northwestern Ontario. Fish. Res. Bd. Can. Tech. Rep. 337: 51 pp.

Koivo, L.K. and J.C. Ritchie. 1978. Modern diatom assemblages from lake sediments in the boreal-arctic transition region near the Mackenzie Delta, N.W.T. Canada. Can. J. Bot. 56: 1010-1020.

Kramer, R.J. 1975. Geochemical and lithological factors in acid precipitation. In Proceedings of the First International Symposium on acid precipitation and the forest ecosystem. United States Forest Service General Tecnical Report. NE 23: 611-618.

Kramer, R.J. and A. Tessier. 1982. Acidification of aquatic systems: a critique of chemical approaches. Environ. Sci. and Technol. 16: 606-615.

Kwiatkowski, R.E. and J.C. Roff. 1976. Effects of acidity on the phytoplankton and primary productivity of selected northern Ontario lakes. Can. J. Bot. 54: 2546-2561.

Likens, G.E. and F.H. Bormann. 1974. Linkages between terristrial and aquatic ecosystems. BioScience. 24: 447-456.

Likens, G.E., R.E. Wright, J.N. Galloway and T.J. Butler. 1979. Acid rain. Scientific American. 241: 43-51.

McNicol, D. 1980. Summary report on the analysis of exiisting precipitation and lake water chemistry water data in the Wawa area of northern Ontario, with particular reference to the feasibility of the area for proposed acid rain studies by the Canadian Wildlife Service in 1980. Canadian Wildlife Service, Ottawa, Ontario.

Merilainen, J. 1967. The diatom flora and the hydrogen-ion concentration of the water. Ann. Bot. Fen. 4: 51-58.

Merilainen, J. 1969. Distribution of diatom frustules in recent sediments of some meromictic lakes. Mitt. Internat. Verein. Limnol. 17: 186-192.

Merilainen, J. 1971. The recent sedimentation of diatom frustules in 4 meromictic lakes. Ann. Bot. Fenn. 8: 160-176.

Merilainen, J., P. Huttunen, and K. Pirttiala. 1982. The effect of land use on the diatom communities in lakes. Hydrobiologia. 86: 99-103.

Munch, C.S. 1980. Fossil diatoms and scales of chrysophyseae in the recent history of Hall Lake Washington. Freshwater Biology. 10: 61-66.

Nriagu, J.O., H.K.T. Wong and R.D. Coker. 1982. Deposition and chemistry of pollutant metals in lakes around the metal smelters at Sudbury, Ontario. Environ. Sci. Technol. 16: 551-560.

Norton, S.A., R.B. Davis and D.F. Brakke. 1981. Responces of northern New England Lakes to atmospheric inputs of acids and heavy metals. Land and Water Resources Center Project Report, A-048-ME. University of Main at Orono. 90 pp.

Nygaard, G. 1956. Ancient and recent flora of diatoms and chrysophyceae in Lake Gribso. Folia Limnologica Scandinavia. 8: 32-99, 254-262.

Partick, R. 1970. Part IX. The diatom in Ianula, an account of the history and development of the Lago di Monterosi, Letrium, Italy. Trans. Amer. Phil. Soc. 60: 112-122.

Patrick, R. and C.W. Reimer. 1966. The Diatoms of the United States. Vol 1. The Academy of Natural Sciences of Philadelphia. 13. 688 pp.

Patrick, R. and C.W. Reimer. 1975. The Diatoms of the United States. Vol 2. The Academy of Natural Sciences of Philadelphia. 13. 213 pp.

Pye, E.G. 1969. Geology and Senery: North Shore of Lake Superior. Ontario Dept. of Mines. 148 pp.

Rawson, D.S. 1956. Algal indicators of trophic lake types. Limno. Oceanogr. 1: 18-25.

Renberg, I. and T. Hellburg. 1982. The pH history of lakes in southwestern Sweden, as calculated from the subfossil diatom flora of the sediments. Ambio. 11: 30-33.

Robinson, R.M. 1980. Acid rain - the crossroad for decision making. J. of Air Pollution Control Federation. 30: 106-108.

Round, E.E. 1957. The late-glacial and post glacial diatom succession in the Kentmere Valley deposits. New Phytologist. 56: 98-126.

Round, E.E. 1964. The diatom sequences in lake deposits: Some problems of interpretation. Verh. Internat. Verein. Limnol. 15: 1012-1020.

Scheider, W.A., D.S. Jeffries and P.J. Dillon. 1979. Effects of acid precipitation on precambrian freshwaters in southern Ontario. J. Great Lakes Res. 5: 45-51.

Scheider, W.A., J. Adamski and M. Paylor. 1975. Reclamation of acidified lakes near Sudbury, Ontario. Ontario Ministry of the Environment.

Schindler, D.W, R.W. Newbury, K.G. Beaty, J. Rrokopowich, T. Ruszchnski and J.A. Dalton. 1980. Effects of a windstorm and forest fire on chemical losses from forested watersheds and on the quality of receiving streames. Can J. Fish. Aqua. Sci. 37: 328-334.

Schofield, C.L. and J.N. Galloway. 1977. The utility of paleolimnological analyses of lake sediments for evaluating acid precipitation effects on dilute lakes. Research Project Technical Completion Report, No. A-071-N.Y. Office of Water Research and Technology, U.S. Department of Interior. 23 pp.

Shannon, J.D. and E.C. Voldner. 1982. Estimation of wet and dry deposition of pollutant sulfur in eastern Canada as a function of major source regions. Water, Air and Soil Pollution. 18: 101-104.

Sparling, J.H. and C. Nalewajko. 1970. Chemical composition and phytoplankton of lakes in southern Ontario. J. Fish. Res. Bd. Can. 27: 1405-1428.

Stewart, A.J. and R.G. Wetzel. 1981. Dissolved humic materials: photodegradation, sediment effects, and reactivity with phosphate and calcium carbonate precipitation. Arch. Hydrobiol. 92: 265-286.

Stinnissen, P. 1975. Report to the Ontario Ministry of Natural Resources, Wawa District. Unpublished. 34 pp.

Stockner, J.G. 1971. Priliminary characterization of lakes in the Experimental Lakes Area, northwestern Ontario, using diatom occurrences in sediments. J. Fish. Res. Bd. Can. 28: 265-275.

Stoermer, E.F. and J.J. Yang. 1969. Plankton diatom assemblages in Lake Michigan. Univ. Mich. Great Lakes Res. Div. Spec. Pap. 47. 268 pp.

Stoermer, E.F. and Y.Y. Yang. 1970. Distribution and relative abundance of dominant plankton diatoms in Lake Michigan. Univ. Mich. Great Lakes Res. Div. Pub. 16. 64 pp.

Stoermer, E.F., S.M Taylor and E. Callender. 1971. Paleolimnological interpretation of the holocene diatom succession in Devil's Lake, North Dacota. Amer. Micros. Soc. Trans. 90: 195-206.

Thode, H.G. and M.D. Dickman. 1983. Sediment sulfur distribution and its relationship to lake acidification in four lakes north of Lake Superior. Progress Report to Environment Canada. 63pp.

Thompson, I. 1980. Acid lakes north of Lake Superior integrated studies in the Wawa area, District of Algoma, to examine the effects of acid precipitation. Ont. Geol. Sur. Misc. Paper 96.

Tyler, G. 1978. Leaching rates of heavy metal ions in forest soil. Water, Air and Soil Pollution. 9: 137-166.

Van Dam, H., G. Suurmond and C.J.F. Braak. 1981. Impact of acidification on diatoms and chemistry of Dutch moorland pools. Hydrobiologia. 83: 425-449.

Van Dam, H. and H.K. Blokland. 1978. Man-made changes in some Dutch moorland pools, as reflected by historical and recent data about diatoms and macrophytes. Int. Revue. ges. Hydrobiol. 63: 587-607.

Vaughan, H.H., J.K. Underwood and J.G. Ogden III. 1982. Acidification of Nova Scotia lakes, I: Response of diatom assemblages in the Halifax area. Water, Air and Soil Pollution. 18: 353-361.

Vermeulin, A.J. 1978. Acid precipitation in the Netherlands. Environ. Sci. Tech. 12: 1016-1021.

Wright, R.F. and E.T. Gjessing. 1976. Acid precipitation: changes in the chemical composition of lakes. Ambio. 5: 219-223.

Yan, N.D. 1979. Pytoplankton communities of an acidified heavy metal contaminated lake near Sudbury, Ontario : 1973-1977. Water, Air and Soil Pollution. 11: 43-45.

Yan, N.D. and P. M. Stokes. 1976. The effects of pH on lake water chemistry and phytoplankton in a LaCloche Mountain lake. Proc. 11th Can. Symp. of Wat. Pollut. Res. in Canada. 127-137.